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(Abstracts section only—see January issue, page 2)

NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc, should consult pages 1–8 of the January 1961 and pages 389–396 of the July 1960 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138). *Editorial Communications* should be addressed to *The Editor*, at the same address.

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Proceedings of the Society

The Biological Chemistry of Cellulose

J. A. Gascoigne

*Meeting of the Manchester Section held at The Textile Institute, Manchester, on 19th February 1960,
Mr. H. A. Turner in the chair*

The rôle of biological catalysts in the breakdown of celluloses and hemicelluloses is discussed. Whereas micro-organisms readily degrade crystalline celluloses, the isolated enzymes only effect hydrolysis of the more accessible amorphous regions; the possibility exists of at least two types of enzyme being active in cellulose hydrolysis. Methods of preventing biological degradation are described, and particular attention is given to substitution and resinification. In the biosynthesis of cellulose, a nucleotide is a likely intermediate, and studies of cell-wall removal from cellulose-synthesising bacteria reveal that the cell wall plays an important part. Hopes are entertained of producing some modification of cellulose during its growth in the plant.

In the Golden Jubilee year of the Society of Dyers and Colourists, the late Sir Norman Haworth[1] presented a lecture on "The Constitution of Cellulose", and it is a great tribute to Haworth's ability that the chemical structure then proposed still holds good. In the natural state, cellulose is associated with many other substances, notably the hemicelluloses, such as xylans and arabans. However, cellulose is not the only polysaccharide to be made up of glucose units linked together in the β-position; such β-glucans occur in cereals, seaweeds and micro-organisms, as can be seen in Table I. Cellulose itself is not confined to the well-known textile sources (e.g. cotton, flax, jute), for bacteria of the genus *Acetobacter* and certain

sea animals also produce cellulose. Indeed, it has been shown recently[2] that some mammalian tissues contain this polysaccharide. The breakdown of these carbohydrates by biological agents has great importance for all textile, paper, and wood processors, and the textile literature reveals many methods for the rotproofing of cellulosic fibres against such ravages.

BIOLOGICAL CATALYSTS

In order to understand the mechanism by which cellulose can be broken down, it is necessary to picture the organisms causing the degradation as catalysts, or as being capable of producing catalysts, for the hydrolysis or oxidation of

TABLE I

Occurrence of β-Glucans

Substance	Principal linkages	Other linkages	Other units	Occurrence
Lichenan	1→3 30% 1→4 70%	—	—	Lichens
Laminarin	1→3	1→6	Mannitol (ca. 2%)	Seaweeds
Callose	1→3	—	Uronic acid (2%)	Grape vines
Oat glucan	1→3 30% 1→4 70%	—	—	Oat grain
Barley glucan	1→3 50% 1→4 50%	—	—	Barley grain
Pustulan	1→6	—	—	Lichens
Pachyman	1→3	—	—	*Poria sclerotia*
Yeast glucan	1→3	1→2	—	Yeast cell walls
Pneumococcus type III polysaccharide	1→3 50% 1→4 50%	—	Glucuronic acid (50%)	*Pneumococci* capsules
Luteic acid	1→6	1→3, 1→4	Esterified malonic acid	Fungi (*Penicillium*)
Crown gall polysaccharide	1→2	?	—	*Phytomonas tumefaciens*
Mung bean seedlings polysaccharide	1→3	—	—	Mung beans

cellulose. Such biological catalysts are called *enzymes*, and are nearly always proteins; they are produced by all living organisms, and may occur within the cells of the organism or may be secreted by the organism into the medium (e.g. sugar solutions, wood, cotton bolls) from which the organism gets its food. This division of enzyme types leads to their classification as *intracellular* or *extracellular* enzymes. Thus, enzymes are not alive, but can frequently be extracted from cells or cell media, although they can, like all proteins, be easily denatured by the application of high temperatures, certain organic solvents, and some types of radiation. As catalysts, enzymes are regenerated at the end of the catalysed reaction, and can then catalyse a repetition of the reaction. Enzymes are specific in their affinity for the reactants: for example, the β-glycosidases catalyse the hydrolysis of β-glycosides, such as cellobiose or xylan, but they have no action in the hydrolysis of α-glycosides, e.g. maltose or starch. Some enzymes are even more specific, and catalyse the hydrolysis, oxidation, reduction, or synthesis of only one compound.

For many years textile chemists have used crude enzymes for assistance in the removal of starch and protein sizes, and such amylases and proteases find analogues in cellulases and hemicellulases which act in the hydrolysis of polysaccharides. One of the purposes of research at the British Rayon Research Association has been to separate cellulases and hemicellulases and so obtain, more specifically, a xylanase acting in the hydrolysis of xylan only and a cellulase catalysing the hydrolysis of cellulose, but not that of xylan. The similarity in the chemical structure of these compounds will emphasise the difficulty of achieving such a result (Fig. 1). A xylanase without action on cellulose has been prepared from the fungus *Fusarium roseum* [3], but no success with the preparation of a pure cellulase has yet been achieved. However, a cellulase preparation from snails was obtained in Cambridge [4] which had no action on xylan, although it acted on mannan, laminarin and yeast glucan. A cellulase produced by Whitaker in Canada [5] and claimed to be a homogeneous protein, had hydrolysing action on both cellulose and xylan [6].
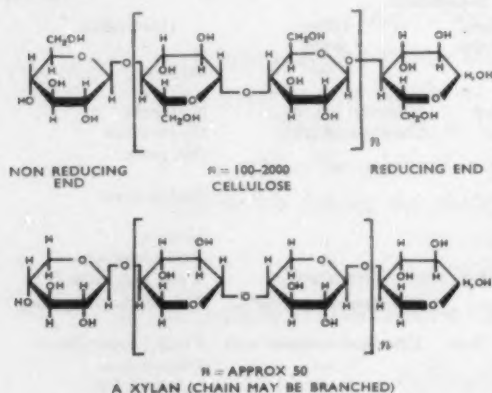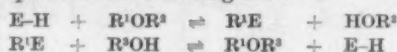

NON REDUCING END   n = 100–2000   CELLULOSE   REDUCING END

n = APPROX 50
A XYLAN (CHAIN MAY BE BRANCHED)

FIG. 1— Chemical structure of cellulose and xylan

In general, an enzyme (E–H) acting on glycosides participates in the following reactions—

$$E\text{–}H + R^1OR^2 \rightleftharpoons R^1E + HOR^2$$
$$R^1E + R^3OH \rightleftharpoons R^1OR^3 + E\text{–}H$$

where the glycoside R^1OR^2 is known as the substrate and R^3OH is the acceptor or receptor, while the structure R–E is the enzyme–substrate complex. If $R^3 = H$, the acceptor molecule is water, and the reaction is hydrolysis of the glycoside R^1OR^2. Thus, R^1OR^2 may represent a simple glucoside, e.g. methyl glucoside, or a polysaccharide such as starch or cellulose. The repeating unit of the cellulose chain is derived from the disaccharide cellobiose, and it is theoretically possible by enzymic hydrolysis to cleave cellobiose units from either the reducing or the non-reducing end of the chain; another type of attack may also be envisaged, by the random cleavage of the chain at several places, giving rise to glucose, cellobiose, and higher oligosaccharides. Many fungi (moulds, mildews) secrete the enzyme cellulase into the substances on which they are growing, and it is this extracellular enzyme that is responsible, to a large extent, for the microbial decay of wood, paper, and cellulosic textiles. The soluble sugars produced by this extracellular action are absorbed by the fungus, and intracellular enzymes then catalyse reactions leading to the build-up of fungal mycelium protein, fatty acids, and carbon dioxide. Although some fungi attack all kinds of cellulose, the cellulase enzyme prepared from them has little action on highly crystalline celluloses, e.g. cotton or ramie.

This peculiarity of the isolated enzyme requires further consideration; the action of isolated cellulase on cotton results in hydrolysis of only 0·2–6% of the sample. Evidently, there must be some loss in cellulolytic activity in isolating such enzymes in the laboratory from the fungal culture medium. Many enzymes are heat-labile, and this loss of activity has been attributed to the denaturation of the enzyme protein, but other important factors are the localisation of the enzyme at the surface of the microbial cell, and the concentration of the enzyme at the site of attack. Reese and his co-workers [7, 8] suggested that two enzymes are necessary for the hydrolysis of cellulose— the C_1-enzyme, which catalyses the production of linear chains from the highly crystalline, hydrogen-bonded native celluloses, and the C_x-enzyme, which degrades the linear chains to small, water-soluble molecules. The C_1-enzyme has not been isolated from a cell-free culture medium, and it seems probable that this enzyme is located very close to, or even attached to, the microbial cell surface. Thus, the activity of the C_1-enzyme can be measured only by using the micro-organism itself, although a similar activity has been measured in some culture filtrates, and has been described as "S"-factor (S for swelling) activity. A very short incubation of cotton fibres with such filtrates induces a marked increase of up to 200% in the subsequent swelling of the fibres in alkali [9]. It may be that S-factor and C_1-enzyme (they may be the same enzyme) are merely the components of the cellulase system which act on

the longest cellulose chains. The C_x-enzyme also catalyses the hydrolysis of many substituted derivatives of cellulose; the reduction in viscosity of carboxymethylcellulose solutions in the presence of the enzyme is used as a measure of enzymic activity.

PREVENTION OF BIOLOGICAL DEGRADATION

In considering the effects of cellulase on cellulosic textiles, wood, and paper, it is not intended to discuss rotproofing at length, but to draw attention to the principal ways in which protection can be afforded. The microbial degradation of cellulose has been adequately described by Siu [10], while a more recent book [11] lays emphasis on the enzymic activities of biological agents such as micro-organisms, insects, molluscs, and plants. Four major forms of protection can be envisaged—

(a) by modifying the cellulose molecule to render it resistant to the action of organisms and enzymes

(b) by imposing a continuous inert physical barrier between the cellulose surface and the deteriorative agency

(c) by treating the cellulose with a toxic agent

(d) by treating the cellulose with a specific enzyme inhibitor.

Each of these processes must fulfil very stringent requirements, apart from efficiency in proofing, such as having no effect on the handle, drape, colour fastness and light fastness of the fabric.

As far back as 1920, Dorée noticed that cellulose acetate resisted microbial attack; other methods of protection have been methyleneation, esterification with aliphatic acids, cyanoethylation, phosphorylation and phosphonomethylation. Early workers believed that one substituent per anhydroglucose unit was necessary to render cellulose resistant to attack. Recently, it has been shown [12] that cellulose modified by substitution with hydrazine, hydroxylamine, and particularly phenylhydrazine, supported very little mould growth at as low a degree of substitution as one substituent molecule per 270 anhydroglucose units. The minimum degree of substitution (D.S.) for conferring mould resistance on cotton has been studied by Reese [13], who obtained the values shown in Table II. However, care must be exercised in considering these values, as the final mildew resistance may well depend on the process by which the substitution reaction is carried out; for example, if, during the reaction, swelling of the fibre occurs, a greater degree of substitution will be necessary. Cotton methylated with diazomethane to a degree of substitution of 0·7 was rot-resistant, whereas if the same degree was achieved with dimethyl sulphate and alkali treatment, the product was not protected [14].

Aminoplast resins provide an inert barrier to some extent, and any excess of formaldehyde present may constitute a toxic agent against mould attack. If cross-linking of such resins with cellulose occurs, as seems probable, all four modes of protection may be provided, since formaldehyde

TABLE II
Degree of Substitution (D.S.) of Cotton Required for Protection[13]

Substitution method	Minimum D.S.
Methylation	0·7
Acetylation	0·5–0·7
Cyanoethylation	0·5
Formaldehyde	0·2–0·3
Phosphate + urea	0·25
Periodate + phenylhydrazine	0·004

inhibits some enzymic reactions. The effectiveness of formaldehyde, and of urea– and melamine–formaldehyde resin treatments on viscose rayon yarns is shown in Table III, in terms of the residual strength after incubation with a potent source of cellulolytic micro-organisms. Even better results were obtained with phenolic resins on viscose rayon yarns, and the halogenated phenol–formaldehyde resins were particularly effective [15]. Recent work [16] has demonstrated the utility of phenolic resins on cotton fibres, although here no advantages were claimed for the halogenated resins.

TABLE III
Strength of Yarns Treated with Formaldehyde, Urea–Formaldehyde (U–F) and Melamine–Formaldehyde (M–F) Resins, and Incubated in Horse-dung Liquid Extract

Time of incubation (days)	No proof	Residual strength (%) 6% M–F	5% U–F	1·6% HCHO
0	100	100	100	100
4	69·3	84·8	98·8	89·8
7	53·8	55·6	83·7	113·9
14	35·4	28·7	67·7	85·0
21	17·0	19·8	41·1	78·7
28	11·3	11·6	35·1	73·9
45	0	6·6	18·5	71·2
65	—	0	13·7	68·0
100	—	—	2·2	53·7
140	—	—	0	44·1

BIOLOGICAL SYNTHESIS OF CELLULOSE

Consideration will now be given to the way in which cellulose is built up in nature. Analytical studies of the carbohydrates in the developing cotton boll suggest that a hexose phosphate is involved in cellulose synthesis [17]. In the laboratory, the bacterium *Acetobacter* forms a very convenient source for the study of cellulose synthesis. The growth of such bacteria on aqueous media containing sugars (e.g. glucose, fructose, sucrose) produces a tough, leathery pellicle of cellulose in which the bacterial cells are enmeshed. The bacterial cellulose is substantially free from the hemicelluloses and lignin found in plant tissues. In both cotton and bacterial cellulose, radioactive glucose supplied during growth was not simply polymerised into cellulose; the glucose was first broken down and the ^{14}C-labelling was not in the same positions in the anhydroglucose units of the final cellulose as in the original monosaccharide [18, 19]. However, 60–80% of the carbon in the 1 position of the glucose was retained at the same position in the anhydroglucose units.

The hexose phosphate intermediate suggested above may well be the nucleotide uridine diphosphate glucose (UDPG) (structure shown in Fig. 2),
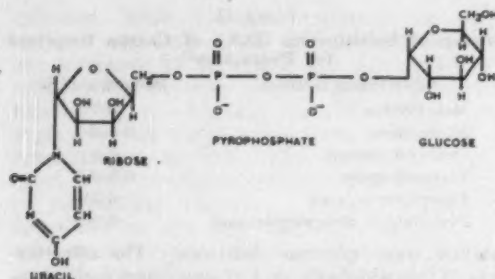
FIG. 2—Structure of uridine diphosphate glucose (UDPG)

which occurs in plants, yeasts and bacterial cells, and is an intermediate in many other poly-saccharide syntheses[20]. The bacterial cell, like that of a fungus, contains intracellular enzymes, and also liberates extracellular enzymes into the surrounding medium. At the British Rayon Research Association, it has been shown[21] that the glucose part of UDPG is not incorporated into bacterial cellulose by the extracellular enzymes, and this has also been proved by workers else-where[22, 23] who used a different species of bacteria. However, with broken bacterial cell extracts containing the intracellular enzymes, Glaser[24] has been able to show that UDPG can be utilised in the synthesis of cellulose.

These considerations led us to look at the structure of the bacterial cell. This cell consists of three layers— an outer cell wall, a thin cytoplasmic membrane, and the protoplasm inner-most, containing the intracellular enzymes and reproductory apparatus. As the *Acetobacter* cell is only $2 \cdot 5 \mu$ long and about $1 \cdot 5 \mu$ in diameter, dis-section of the cell can only be done chemically. First, growth of these bacteria in the presence of penicillin leads to the inhibition of cell-wall formation in successive generations of bacteria. Alternatively, the cell wall may be "etched" away (actually, partially hydrolysed) with the aid of the enzyme lysozyme and a chelating agent (EDTA). Such partial removal of the cell wall makes the cell lose its rigidity, and the normal rod-shaped cell becomes spherical and very fragile. However, such spherical "cells" or protoplasts can be isolated in the presence of a stabiliser (high con-centrations of polyethylene glycol or sucrose), and they do not then form cellulose[21]. Clearly, the cell wall must play some part in cellulose biosyn-thesis. At present, attempts are being made to isolate the cell wall itself by ultrasonic disintegra-tion of the cell. At this stage, all that can be said is that the extracellular enzyme system and its substrate can be obtained by alcohol extraction of growing cells[21, 22], but the structure of this extra-cellular substrate or precursor of cellulose is unknown; Colvin in Ottawa is working on this problem.

At very early stages of growth (6–48 hours), bacterial cellulose resembles an almost transparent gel, with a very high water content. It was thought that this gel might contain amorphous cellulose, but studies of growth in heavy water, and infrared spectroscopy[25] of the deuterated 40 hour-old cellulose, have led us to conclude that even this

"gel"-cellulose is highly crystalline. At the present time, Dr. A. M. Brown and I are investigating the changes in degree of polymerisation of cellulose during the early stages of growth, the influence of glucose concentration on cellulose yield, and the role of possible primer molecules (such as cello-tetraose, cellobiose-1 phosphate) in the formation of the high polymer.

HOPES FOR THE FUTURE

If the process of cellulose formation is known, there is a possibility of producing some modification of the cellulose during its growth by the plant, and thus enabling the cotton or flax plant to give the textile manufacturer a "tailor-made" fibre of known (and desirable) crystallinity, degree of polymerisation, degree of substitution, and chemical structure. This object has been achieved to a large extent in the growth of amylopectin for textile sizes by genetic control of corn plants, and genetic control has already improved the cotton plant. Therefore, in addition to revealing more facts about the physical structure and biosynthesis of cellulose, such studies may ultimately serve as a basis for the production of new, but natural, fibres.

* * *

Some of the studies described here were com-menced in the Department of Chemistry at the University of Birmingham with Professor M. Stacey, F.R.S., and in the Department of Textile Industries at the University of Leeds with Dr. J. W. Bell and Professor C. S. Whewell. The author wishes to acknowledge the help and advice of the Director and colleagues at the British Rayon Research Association.

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COMMUNICATIONS

The Absorption of Saturated Azobenzene Vapour by Cellulose Acetate

F. JONES

The rates of absorption of saturated azobenzene vapour by cellulose acetate film have been measured over a range of temperatures by means of a completely enclosed silica spring balance. The results indicate that diffusion is "anomalous" or non-Fickian below the upper second-order transition temperature (120°C) of cellulose acetate. Apparent diffusion coefficients were found to vary with concentration, and the activation energy of diffusion increased to a constant value of $+31 \cdot 0$ kcal/mole as the concentration of azobenzene in the film increased. This variation of the apparent diffusion coefficient is attributed in part to the energy required for "hole" formation in the polymer and in part to the increased mean free path of the diffusion species. Saturation values in the cellulose acetate were higher than those obtained by conventional dyeing methods, and it is concluded that the process of vapour-phase absorption differs fundamentally from the process of absorption from aqueous systems.

Introduction

Although much experimental work has been reported [1-4] on the sorption of water vapour by secondary cellulose acetate, the sorption of organic vapours has been confined mainly to the work of Long and co-workers [5-7], who have used simple organic compounds possessing appreciable vapour pressures. The rates of absorption of these vapours may be increased by raising the temperature of the system, but this increase is limited with cellulose acetate, which can undergo structural changes at high temperatures, especially in the presence of absorbed molecules. These structural alterations are indicated by a discontinuity in the rate of change of a property (e.g. specific volume or heat capacity) of the polymer with temperature, the temperature at which this discontinuity occurs being known as the apparent second-order transition temperature or glass temperature. It is now generally accepted that, above this temperature, diffusion of small organic molecules into a polymer film usually follows Fick's Law, and below this temperature, i.e. in the glassy state, diffusion is often "anomalous" or non-Fickian, unless the concentration of vapour molecules is very low.

Mandelkern and Flory [8] have reported two apparent second-order transitions for cellulose acetate, characterised by sudden changes in specific volume, at 60°C and 120°C. It was considered of interest therefore to study rates of absorption between these two temperatures and to use more complex molecules, in particular disperse dyes or "model" compounds bearing a close structural resemblance to either aminoanthraquinone or azo disperse dyes. Such substances have a small but definite vapour pressure [9], and are absorbed by cellulose acetate from the vapour [10]. The vapour pressures of some "model" compounds, including azobenzene, have been measured by Majury [11], who has also determined the heats of association between cellulose acetate and the vapours of these substances. As far as is known, the kinetic approach to the system solid dye–dye vapour–absorbed dye has not previously been studied. Azobenzene was chosen because its vapour pressure is known and preliminary experiments had shown that the equilibrium saturation value could be obtained in a comparatively short time at temperatures between 80 and 120°C.

Experimental

MATERIALS

Azobenzene (analytical reagent grade) was recrystallised from methyl alcohol until a constant m.p. was obtained. Sufficient for experimental use was sublimed (m.p. 68·0°C corr.) and stored in an evacuated glass tube in the dark until required.

The cellulose acetate powder was a commercial grade (Lansil Ltd) with a combined acetic acid content of 53·8%. A 5% (wt./vol.) solution of the powder in dry redistilled acetone was cast on glass, as described by Daruwalla and Turner [12], after centrifuging the solution to remove a small amount of undissolved fibrils. The film was leached in distilled water for several days to remove residual solvent [5] and conditioned at 65% r.h. and 22°C. The thickness of the film was calculated from the area and weight of several oven-dried discs cut from random portions of the film, the diameters being measured by means of a cathetometer. The mean thickness, assuming a density of 1·31 g/cm³ for the dry polymer, was found to be 18·4($\pm$0·6) μ.

APPARATUS

Approx. 70–80 mg of conditioned film were accurately weighed in a weighing bottle on a semi-micro analytical balance, and transferred to a previously calibrated McBain and Bakr [13] silica spring balance. Calibration was achieved by the addition of small, accurately known glass weights, the load–extension curve being linear over the working range. The provision of two silica spring
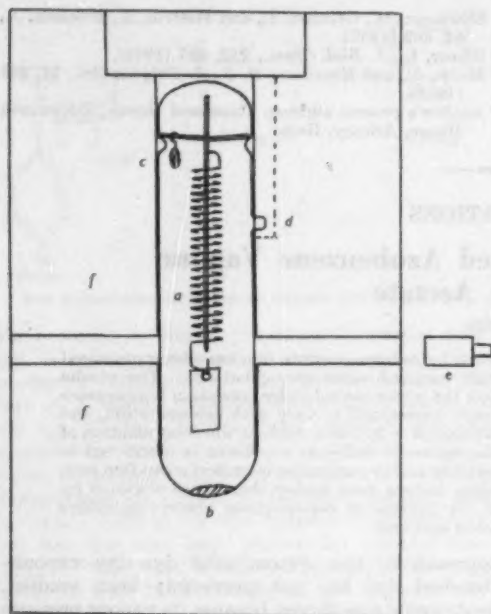
FIG. 1— Sorption balance and thermostat

balances allowed one to be prepared while the other was in use.

The film-loaded balance (a— Fig. 1) was transferred to the balance case containing solid azobenzene (b). A small thin-walled glass capsule (c) containing uranyl acetate, necessary to discharge any static electricity which might develop on the spring, was also enclosed. The top was sealed, and the balance case evacuated for over 6 h at a pressure of $< 5 \times 10^{-6}$ mm mercury and sealed at d. It was then placed in an electrically heated Duralumin block thermostat (f). Temperatures inside the block could be controlled to within ± 0.2 degrees up to 170°C. The apparatus was adjusted so that the spring tip and the tip of the central zero rod were in the same focal plane when viewed through the cathetometer (e). The thermostat was rapidly heated to the required temperature

and readings of the spring deflection were immediately begun. The deflection was observed through a mica window, 1 cm in diameter, the cathetometer reading to ± 0.001 mm. All measurements were referred to the tip of the zero rod in order to overcome any errors introduced by movement of the cathetometer or apparatus. Readings were continued until no further extension of the spring could be observed. Rates of absorption of saturated azobenzene vapour were measured over the temperature range 80–100°C.

During this absorption period no chemical changes in the substrate were observed. This was confirmed by heating samples of film in vacuo at 140°C for up to 200 h. When the method of Howlett and Martin [14] was used, no change in acetic acid content outside the limits of experimental error ($\pm 1.5\%$) was detected.

Results

The rates of absorption of saturated azobenzene vapour at temperatures between 80·0 and 99·7°C are shown in Fig. 2, where C_∞ is the equilibrium saturation value and C_t is the total amount of azobenzene vapour absorbed by the film at time t. C_∞ and C_t are expressed in g/100 g anhydrous film. The curves are sigmoidal without the initial linear portion that would be found if the system obeyed Fick's Law.

APPARENT DIFFUSION COEFFICIENTS

The apparent diffusion coefficients (D_a) for this family of curves were obtained by the use of the McBain equation [15] for non-steady state diffusion—

$$C_t/C_\infty = 1 - \frac{8}{\pi^2}\left(e^{-A} + \frac{1}{9}e^{-9A} + \frac{1}{25}e^{-25A} + ..\right) ... (1)$$

where $A = \pi^2 D_a t/b^2$, and b is the thickness of the film. C_t and C_∞ are defined above.

Values of $D_a t/b^2$ for known values of C_t/C_∞ at different times are given by Vickerstaff [16]; D_a has been calculated from a graph of these values. Values of D_a obtained from eqn. (1) were not constant, but increased linearly with increases in the concentration of absorbed azobenzene, as shown in Fig. 3. The greatest increase was observed at the highest temperature.

1— 99·7°C   4— 84·9°C
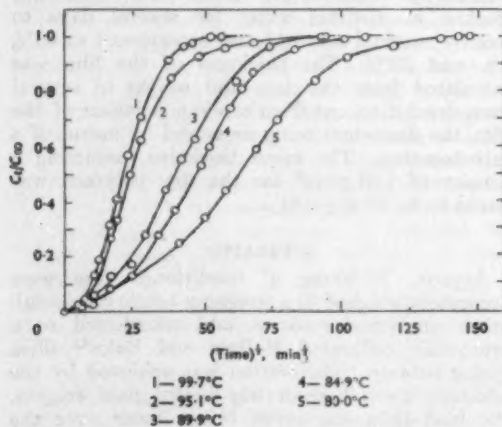2— 95·1°C   5— 80·0°C
3— 89·9°C

FIG. 2— Absorption curves of saturated azobenzene vapour

1— 99·7°C   4— 84·9°C
2— 95·1°C   5— 80·0°C
3— 89·9°C

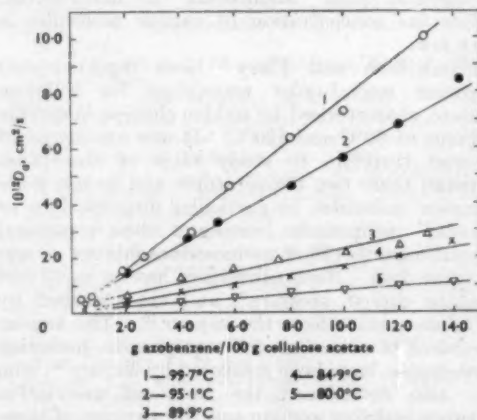FIG. 3— Variation of D_a with concentration of absorbed azobenzene

TABLE I
Apparent Diffusion Coefficients of Azobenzene (cm²/s × 10¹²)

Temp.	Azobenzene concentration (g/100 g anhydrous cellulose acetate)						
°C	1·0	2·0	4·0	6·0	8·0	10·0	12·0
99·7	0·782	1·555	3·101	4·647	6·193	7·739	9·285
95·1	0·753	1·322	2·460	3·598	4·736	5·874	6·846
89·9	0·501	0·693	1·077	1·461	1·845	2·229	2·613
84·9	0·214	0·386	0·730	1·074	1·418	1·762	2·106
80·0	0·169	0·237	0·373	0·507	0·645	0·781	0·917

These results may be expressed in the form—

$$D_a = D(1 + \alpha C_t) \qquad \dots\dots (2)$$

where D is the apparent diffusion coefficient at zero concentration and α is the slope of the D_a vs. C_t curve. Smoothed values of the apparent diffusion coefficients of azobenzene calculated from eqn. (2) are given in Table I. They were obtained by the method of least squares, as were all the gradients in this work. It should be noted that eqn. (2) is an approximation, since variation of the diffusion coefficient with concentration precludes the simple integration of Fick's equation to give eqn. (1). In the film the diffusion coefficient will vary from layer to layer, whereas in eqn. (2) the concentration term is expressed in g/100 g of the whole dyed film.

ACTIVATION ENERGY AND ENTROPY OF DIFFUSION

Diffusion, according to the theory developed by Eyring [17] and co-workers, is an activated process, the activation energy being obtained from the expression—

$$D_a = D_0 \exp(-E/RT) \qquad \dots\dots (3)$$

where E is the activation energy of diffusion and D_0 is a constant. This can be rewritten as

$$\log_e D_a = \log_e D_0 - E/RT$$

so that E may be calculated from the slope of the $\log_{10} D_a$ against $1/T$ curve—

$$E = -2\cdot303R \cdot \frac{d(\log_{10} D_a)}{d(1/T)}$$

Values of E at several arbitrary concentrations of azobenzene in the film have been calculated from these plots and are shown in Table II, together with the corresponding values of D_0 obtained from the intercepts of these curves with the ordinate axis.

TABLE II
Activation Energies and Entropies of Diffusion

Azobenzene concn. g/100 g cellulose acetate	E kcal/mole	D_0 cm²/s	ΔS_d^* cal/mole /deg.
1·0	23·1 (±3·3)	3·51 × 10⁻¹	0·59
2·0	26·7 (±2·4)	8·18 × 10²	20·60
4·0	29·1 (±1·9)	4·17 × 10⁴	28·40
6·0	30·0 (±2·3)	2·01 × 10⁶	31·52
8·0	30·6 (±2·5)	6·01 × 10⁶	33·70
10·0	31·0 (±2·6)	1·19 × 10⁷	35·05
12·0	31·0 (±2·7)	1·61 × 10⁷	35·66

E increases rapidly as the concentration of absorbate within the film builds up, but approaches a constant value as equilibrium is approached.

During the initial stages of absorption, not recorded in Table II, the activation energy is < 23 kcal/mole, although the large scatter of experimental points at low concentrations does not allow an accurate value to be calculated. Values of the initial slopes of the absorption curves (Fig. 2) indicate a value ~16 kcal/mole for E at concentrations of $< 1\cdot0$ g/100 g cellulose acetate.

Since diffusion is not generally accompanied by a change in volume, it is possible to replace eqn. (3) by

$$D_a = e\lambda^2 \frac{kT}{h} \exp(\Delta S_d^*/R) \exp(-E/RT)$$

where λ is the distance between successive equilibrium positions of the absorbed molecule in the substrate, ΔS_d^* is the entropy of activation of diffusion and k and h are the Boltzmann and Planck constants. It follows that D_0 in eqn. (3) is given by

$$D_0 = e\lambda^2 \frac{kT}{h} \exp(\Delta S_d^*/R) \qquad \dots\dots (4)$$

and, if λ is estimated, values for ΔS_d^* can be found. For the diffusion of C_4- and C_5-hydrocarbons into ethylcellulose, Barrer, Barrie, and Slater [18] have used a value of 11 Å for λ. Substitution of this value in eqn. (4) gives the values of ΔS_d^* at 100°C listed in Table II.

EQUILIBRIUM SATURATION VALUES

The amounts of azobenzene vapour absorbed at equilibrium (C_∞) by anhydrous cellulose acetate are given in Table III. The range of temperatures has been extended, although above 99·7°C rates of absorption were not measured. The temperature of the balance case containing solid azobenzene and cellulose acetate film, previously vapour-dyed to equilibrium at 99·7°C, was raised to 104·3°C and equilibrium re-established. The process was repeated at temperature intervals up to 129·2°C.

TABLE III
Vapour-phase Partition Coefficients (K)

Temp. °C	C_∞ g/100 g cellulose acetate	C_g g/unit vol. × 10⁴	K × 10⁻⁴
80·0	17·39	1·184	14·690
84·9	15·11	2·437	6·201
89·9	15·00	2·551	5·880
95·1	15·70	3·400	4·617
99·7	14·19	4·152	3·418
104·3	14·72*	5·305	2·775
111·8	14·73*	7·801	1·888
120·5	14·52*	11·99	1·211
129·2	13·87*	17·91	0·774

* Mean values.

The temperature was then decreased by the same intervals to 104·3°C. The saturation values obtained during the latter process agreed to within $\pm 2 \cdot 0\%$ with the values obtained in the stepwise increase of temperature. These mean values are shown in Table III.

From thermodynamical considerations the standard free energy change, ΔG°_{abs}, in the transfer of one mole of azobenzene from its standard state in the vapour to its standard state in the substrate is given by

$$\Delta G^{\circ}_{abs} = -RT \log_e (C_{\infty}/C_v) = -RT \log_e K \quad \ldots (5)$$

where K is the partition coefficient between the equilibrium concentration in the film (C_{∞}) and the concentration of saturated vapour (C_v) at temperature T, both values being expressed in identical units. In Table III, C_v is expressed in terms of the weight of vapour (in grammes) in the volume (cubic centimetres) occupied by 100 g of anhydrous cellulose acetate. If it is assumed that the vapour behaves ideally, which is probably true at the low concentrations used, C_v is given by

$$C_v = pM/13\cdot1 \; RT$$

where p is the saturation vapour pressure in atmospheres, R is the gas constant ($0\cdot0819$ litre-atm.deg.$^{-1}$mole^{-1}) and M is the molecular weight. The standard state of azobenzene in the substrate is defined as the state at unit concentration per 100 g anhydrous cellulose acetate, and the standard state in the vapour as the state at unit concentration, i.e. 1 g of vapour in $100/1\cdot31$ cm^3, the factor $1\cdot31$ being the density of anhydrous cellulose acetate in g/cm^3. This amount has been chosen to agree with the unit chosen for concentration in the solid phase.

Since $C_{\infty}/C_v = K$, the partition coefficient in the vapour phase, the standard heat of absorption (ΔH°_{abs}) is given by

$$\Delta H^{\circ}_{abs} = -\frac{d(R \log_e [C_{\infty}/C_v])}{d(1/T)}$$

ΔH°_{abs} is obtained from the gradient of the plot of $\log_{10}(C_{\infty}/C_v)$ against $1/T$, shown in Fig. 4—

$$\Delta H^{\circ}_{abs} = -\text{gradient} \times 2\cdot303 \times R$$

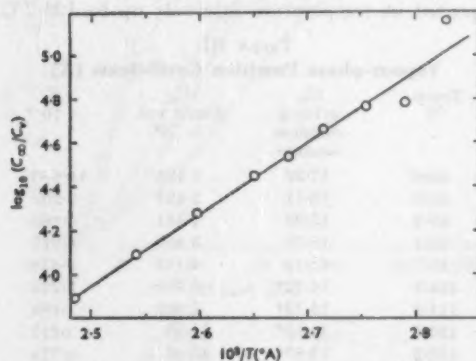
FIG. 4— Relation between $\log_{10}(C_{\infty}/C_v)$ and temperature

By this method the standard heat of absorption of azobenzene vapour is $\Delta H^{\circ}_{abs} = -15\cdot2(\pm 0\cdot9)$ kcal/mole. The heat of sublimation has been given by Majury[11] as 15·5 kcal/mole, so that the heat of solution of azobenzene in anhydrous cellulose acetate is $15\cdot5 - 15\cdot2 = 0\cdot3$ kcal/mole. This value is approximate because of the possible errors in the determination of the heat of sublimation and of the heat of absorption.

ENTROPY OF ABSORPTION

The relation between $\log_e K$ and temperature is given by eqn. (6), derived by assuming that the system is ideal and that the heat of absorption is temperature independent—

$$\log_e K = -\Delta H^{\circ}_{abs}/RT + c \quad \ldots (6)$$

The standard entropy change (ΔS°_{abs}) in the transfer of one mole of vapour in its standard state as previously defined to its standard state in the substrate may be found from

$$\Delta G^{\circ}_{abs} = \Delta H^{\circ}_{abs} - T \Delta S^{\circ}_{abs} \quad \ldots (7)$$

From eqn. (5) and eqn. (7),

$$\Delta S^{\circ}_{abs} = \Delta H^{\circ}_{abs}/T + R \log_e K \quad \ldots (8)$$

Rearranging eqn. (6) and substituting in eqn. (8) gives

$$\Delta S^{\circ}_{abs} = Rc = 2\cdot303 \; Rc'$$

where c' is the intercept on the $\log_{10} K$ vs. $1/T$ plot. The experimental result for the intercept of this plot (Fig. 4) shows that there is a fall in the standard entropy of $19\cdot9(\pm 2\cdot3)$ entropy units (e.u.) in proceeding from the vapour to the substrate. This may be compared with a rise in entropy of $27\cdot7$ e.u. on the transfer of one mole of azobenzene from the solid to the vapour. This gives a value of $+7\cdot8$ e.u. in the direct transfer of azobenzene from its crystalline form to the substrate.

Discussion

The errors involved in the determination of C_t and C_{∞} are mainly those arising from the calibration of the silica springs and the weighing of film samples prior to absorption. The calibrated sensitivity of the less sensitive spring was found to be $1\cdot592(\pm 0\cdot007) \times 10^{-2}$ g/cm. The lowest saturation value obtained could therefore be determined to within an error of $\pm 0\cdot4\%$. These springs were calibrated at room temperature, and it was assumed that the sensitivity would remain constant at higher temperatures. This sensitivity is inversely proportional to r^4, r being the radius of cross-section of the fibre from which the spring has been constructed. For a silica fibre, diameter $0\cdot1$ mm, the increase in r^4 is approx. $0\cdot5\%$ at 170°C. This will account for a decrease in spring sensitivity of $0\cdot5\%$ and a consequent error in the saturation value of $-0\cdot4\%$. Confirmation that the spring sensitivity is unaltered or only slightly altered at high temperatures was indicated by the agreement with the results of Majury[11], who obtained saturation values by dissolution of

vapour-dyed films and photometric estimation of
the resultant solutions. In certain cases it was
possible to check the saturation values of azo-
benzene obtained by the sorption balance method
against the method of dissolution and photometric
estimation, the results agreeing to within $\pm 0.4\%$.
Smaller errors arose in weighing film samples and
were found to be $< \pm 0.1\%$.

Azobenzene in solution can undergo *trans→cis*
rearrangement when exposed to u.v. radiation or
to daylight [20], and the solid *cis* form can be isolated.
The probability that *cis*-azobenzene is present
during the absorption of vapour by cellulose
acetate is negligible, firstly because of the absence
of light, and secondly because the effect of heat is
to cause any *cis*-azobenzene present to revert to
the *trans*-form [21]. Indirect evidence is also pro-
vided by Wyman and Brode [22], who demonstrated
the same effect of heat with thioindigo derivatives,
where rearrangement occurs about the ethylenic
linkage.

KINETICS OF ABSORPTION

The initial portions of the absorption curves for
azobenzene vapour shown in Fig. 2 are non-linear,
in contrast to the linearity predicted by Fick's Law
with constant boundary conditions and a diffusion
coefficient which is dependent on concentration
but does not depend on any other variable [23].
Non-Fickian diffusion, giving rise to sigmoidal
absorption curves, has been attributed [24] to a
variable surface concentration, when the latter
approaches a surface equilibrium concentration
exponentially or linearly with time. This type of
diffusion process has been observed experimentally
by Long and Richman [25] when small organic
molecules are absorbed by cellulose acetate, the
initial low rate of absorption being due to the
possibility of forming a low concentration of
absorbed molecules at the surface of the substrate
which requires time to build up to an equilibrium
saturation value. This may apply to azobenzene
molecules, the initial low surface concentration
being attributable to possible differences in
structure between surface and interior of the film.
Since this sigmoidal behaviour is observed up to
100°C, Fickian diffusion may possibly occur only
above the higher (120°C) transition temperature.
Russel and van Kerpel [26] point out that the
transition at 120°C is the main transition, caused
by the rotation of chain segments, the lower
transition having little effect on the mechanical
properties of the polymer. According to Woods [27],
this lower transition is associated with the mobility
of the acetyl groups. That 120°C is the main
glass temperature is apparent also from the
reduction in the equilibrium saturation values
above this temperature both in the present
research and in Majury's [11] results.

It is generally observed that the second-order
transition temperature is depressed by the presence
of absorbed molecules. It was possible to com-
pare in a separate experiment the transition
temperature of cellulose acetate in both absence and
presence of saturated 1-methylaminoanthraquinone
vapour by observing the extension, under constant

load, of a thin strip of film over a range of tempera-
tures up to 200°C. The results showed a decrease
of 8 degrees in the observed value of 125°C for the
upper transition temperature. From this it is
possible to infer that Fickian diffusion will probably
occur only above the upper second-order transition
temperature of anhydrous cellulose acetate, where
the onset of partial chain rotation facilitates the
ingress of the comparatively large (15Å long)
azobenzene molecule.

The apparent diffusion coefficients of azobenzene
vapour are concentration dependent, as shown in
Fig. 3 and eqn. (2), where the dependence is found
to be linear. A similar equation has been derived
by Hayes and Park [28] for the variation of the
average diffusion coefficient in water–rubber
systems. The variation of D_a with concentration
may arise in several ways—

(*a*) From the use of concentrations instead of
activities in Fick's and McBain's equations.

(*b*) From the variations in mobility or the mean
free path, λ, of the absorbed molecules as their
concentration builds up in the substrate. From
eqn. (4), D_0 is proportional to λ^2, so that the
increase in D_0 shown in Table II may be due to an
increase in λ or in the entropy of activation, or to
increases in both. The values given for ΔS_d^*
assume a constant mean free path and, unless λ is
known accurately, the absolute value for the
activation entropy cannot be obtained, since λ and
ΔS_d^* are inter-related.

(*c*) In non-steady-state diffusion, the con-
centration of the absorbed molecules in the
polymer increases so that in the later stages of
diffusion azobenzene molecules should be con-
sidered to diffuse into an azobenzene–polymer
network and not a network of polymer chains
alone. This will affect the activation energy of
diffusion, since the energy of "hole" formation, i.e.
the energy required to separate the polymer chains
sufficiently to allow the diffusing species to pass,
will most probably change and include a term that
is dependent on the energy of sublimation of the
latter.

HEAT OF ABSORPTION

The amounts of azobenzene absorbed by the
cellulose acetate film at equilibrium are very much
greater than the amounts absorbed during aqueous
dyeing from saturated solutions over the same
temperature range. From microscopic examina-
tion of cross-sections of the film there does not
appear to be any surface excess of azobenzene.
However, if such films are kept under atmospheric
conditions at room temperature, there is a
migration (of azobenzene) to the surface which is
easily visible in crystalline form. This is probably
due to the diffusion of moisture, since films stored
in vacuo at room temperature do not show this
phenomenon.

The experimental heat of absorption of azo-
benzene, -15.2 kcal/mole, is lower than Majury's
experimental value [11] of -17.8 kcal/mole. Majury
compares this experimental value with a value for
the "absolute heat of association" calculated from
the latent heat of sublimation and aqueous dyeing

data. Although the results are of the same order a comparison is not valid, since the substrate is in an anhydrous condition in vapour-phase absorption and no account has been taken of thermodynamical quantities such as the heat of swelling. It must be emphasised that dyeing from the vapour differs fundamentally from aqueous dyeing on these grounds. However, the heat of absorption may be a useful concept in the study of the physical aspects of the Thermosol process [29] or the dyeing of materials *in vacuo* in the presence of dye vapour [30].

SOLUBILITY PARAMETERS

If the absorption of azobenzene by cellulose acetate is regarded as a solution process, the solubility equation developed by Hildebrand and Scott [31] may be applied, in a modified form, to determine the energy of mixing—

$$\Delta E_A^M = V_A (\delta_A - \delta_P)^2 \qquad \dots (9)$$

where ΔE_A^M is the energy of mixing, V_A is the molal volume of azobenzene, and δ_A and δ_P are the solubility parameters of azobenzene and polymer, respectively. It is assumed that the solution of azobenzene in the polymer is dilute. δ_A may be defined as $(\Delta E_A^{sub}/V_A)^{\frac{1}{2}}$, where ΔE_A^{sub} is the energy change on sublimation. δ_P cannot be found by this method, but Moore [32] quotes a value for the solubility parameter of cellulose acetate, determined by the solubility of this polymer in solvents of different δ, of $11\cdot0(cal/cm^3)^{\frac{1}{2}}$ at 25°C. If $\delta_A = \delta_P$, ΔE_A^M is zero, i.e. both components are acting ideally and will mix in all proportions. The value of the term $(\delta_A - \delta_P)$ should therefore give an approximate measure of the efficiency of mixing and be related to ΔH_{sol}°, the standard heat of solution of the compound in the film determined by vapour-phase absorption. Since ΔH_A^M, the heat of mixing of solid azobenzene with solid cellulose acetate, approximates to ΔE_A^M, the former may be compared with ΔH_{sol}° using the value of ΔE_A^M calculated from eqn. (9), the density [33] of azobenzene being $1\cdot22$ g/cm³. By this method the calculated heat of mixing is $0\cdot05$ kcal/mole, compared with the experimental heat of solution of $0\cdot3$ kcal/mole. It is essential that the value of δ_P be known accurately, since an error of, say, 5% in δ_P could cause a large error in the energy of mixing when $(\delta_A - \delta_P)$ is small. Hildebrand states that the equation for the energy of mixing holds reasonably well for polyatomic

and moderately polar molecules, so that the theoretical aspects should be valid for dye and substrate systems under anhydrous conditions if there is a positive energy of mixing.

It appears from both the experimental value and the theoretical value deduced from solubility parameters that the heat of mixing of solid dye and solid polymer to give a solid solution is approximately zero, so that as regards energetics the mixture behaves ideally, although this is not necessarily true as regards the entropy of mixing.

*   *   *

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The Discoloration of Wool Grease in the Recovery Process

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The colour of wool grease varies from yellowish brown to dark brown, and can be attributed partly to the presence of natural pigments and partly to the formation of coloured derivatives of the waxy constituents by autoxidation. Other coloured compounds may be formed during the recovery of grease from the wool-scouring liquors (or the solvent). Observations are reported on the mode of formation of the third group of coloured materials.

Extremely viscous films are formed at the interfaces of heterogeneous systems containing wool wax and suint, particularly between the hydroxy-acids of the wax and the peptides of suint [1]. The interfacial complexes are, of course, insoluble in both phases and are pale in colour, but it will be shown below that they darken when heated, and can make an appreciable contribution to the colour of the wax.

DISCOLORATION OF THE WAX IN THE SOLVENT SCOURING PROCESS

The systems studied are described in Table I. Basically, they consisted of an aqueous solution (1 ml) and a solution of commercially refined lanolin (1 g) in white spirit (50 ml). The solutions were shaken together and allowed to separate. In the system containing α-hydroxypalmitic acid, a flocculent precipitate accumulated between the phases. After the phases had been completely separated by centrifuging the mixture, a sample (25 ml) of the oil phase from each system was withdrawn, the solvent was distilled off under reduced pressure, and the residue was heated to 100°C for 12 hours. A portion of the residue (0·1 g) was made into a standard solution in benzene (10 ml) and the optical density of the solution (against a benzene blank) was measured in the range 390–700 mμ on a Unicam SP500 spectrophotometer. From the area under each spectral trace, the colour of the wax was evaluated in arbitrary units (Table 1).

The residual oil phase, together with the interfacial complex from the system containing α-hydroxypalmitic acid, was washed with water (50 ml), the emulsion was centrifuged, and the clear aqueous layer was drawn off. After this process had been repeated ten times to ensure complete removal of the suint, the white spirit layer was removed and evaporated to dryness, and the residue heated to 100°C for 12 hours. Subsequent determination of the colour of the residue, i.e. the wax plus what was formerly interfacial complex, was carried out as before. It should be noted that at this stage the residue was completely soluble in benzene.

The outstanding feature of these results is the nine-fold increase in the colour of the wax in the system containing the interfacial complex. Heat treatment and mere contact of lanolin with suint are not, by themselves, sufficient to discolour the wax. A brief description of the solvent scouring process will show the importance of the part played by these complexes in the discoloration of the commercial product.

When greasy wool is immersed in white spirit, the wax, a small amount of hygroscopic suint, and the solid dirt are transferred to the white spirit. In this fluid system an interfacial complex is formed, and it is gradually precipitated. Subsequently, the solvent is centrifuged to remove the heavy dirt. As the economic functioning of the process depends largely on the recovery of the solvent, the centrifuge is adjusted to deliver dirt containing the minimum amount of solvent. Because the density of the complex is greater than that of the solvent but less than that of aqueous suint, it will be removed with the solvent. Subsequently, the wax is recovered by vacuum distillation, and it is at this stage that the wax-soluble coloured compounds are formed.

The easiest method of obtaining wax free from this type of discoloration is to sacrifice some of the wax yield. The dirt-free solvent is centrifuged again to obtain a main fraction of clean solution and a minor fraction containing solvent and complex. Clean wax and clean solvent are obtained by distillation of the main fraction, and the minor fraction yields clean solvent and discoloured wax which must be rejected.

DISCOLORATION OF THE WAX IN THE CENTRIFUGAL RECOVERY SYSTEM

In the commercial operation of the centrifugal grease-recovery process, the scouring liquors are first passed through a sludge separator. From the sludge separator an emulsion containing a greater

TABLE I

Discoloration of Lanolin after Contact with Suint

Aqueous phase (1 ml water)	Oil phase (1 g lanolin in 50 ml white spirit)	Colour (arbitrary units)
Additions—	Additions—	
(i) none	none	59
(ii) suint (0·2 g)	none	55
(iii) suint (0·2 g)	palmitic acid (0·1 g)	85
(iv) suint (0·2 g)	α-hydroxypalmitic acid (0·05 g): excluding the interfacial complex	57
(v) suint (0·2 g)	α-hydroxypalmitic acid (0·05 g): including the interfacial complex	540
Commercial lanolin (original sample)		52
α-Hydroxypalmitic acid (heated for 12 h at 100°C)		1

TABLE II
Properties of Waxes Extracted from Liquors in Different Parts of Commercial Centrifugal Grease-recovery Processes

	Grease content of liquor (%)		Nitrogen content of wax (%)		Colour of wax (arbitrary units)	
	Without SSB*	With SSB	Without SSB	With SSB	Without SSB	With SSB
Input	2·6	2·2	0·28	0·18	1340	660
Aqueous concentrate	1·5	1·4	0·35	0·22	1870	660
Grease concentrate	6·5	71	0·28	0·07	610	480
Dirt (reject)	1·4	1·4	0·27	0·25	1440	760

* In the process without a suint-steep bowl (SSB) the input was diluted with hot water.

concentration of grease goes forward to the next centrifuge, a soap-rich aqueous phase is returned to the scouring train, and insoluble materials are rejected. During the processing, the liquors are maintained at temperatures exceeding 70°C for considerable periods.

Waxes from each of these streams from the sludge separator have been analysed for colour and for nitrogen content. One set of samples was obtained from a scouring train in which the suint was dissolved in the liquors which were to be centrifuged, and the other set from a scouring train which contained a preliminary suint-steep bowl. In the latter process, the suint liquors were not mixed with the liquors which were fed to the sludge separator.

The wax was extracted by thoroughly mixing the sample (75 ml) with carbon tetrachloride (78 ml) and ethanol (78 ml), and centrifuging the emulsion until it had been resolved into two clear layers. The bottom layer (carbon tetrachloride) was drawn off and filtered through a sintered-glass crucible (No. 4), and the crucible was washed with carbon tetrachloride (60 ml). Finally, the solvent was removed from the combined filtrate and washings. Colour values were determined as before, and the values in Table II are in the same arbitrary units as those in Table I.

These observations show that the colours of the waxes are loosely correlated with their nitrogen contents although, as was pointed out earlier, the nitrogen derivatives are only one source of discoloration. More important, the results show that a considerable proportion of the coloured materials in the wax are formed after contact with suint; in this series the wax and suint have been in contact and they have been heated together, so that both conditions for discoloration have been fulfilled. The colour of commercially recovered wool grease can be improved if two precautions are taken. First, wax and suint should not be brought into contact in a heterogeneous system, and secondly, if the formation of interfacial complexes is unavoidable, they should not be heated in the presence of the wax. The first precaution has already been advocated in connection with improvements in the efficiency of recovery [1], and now its importance in connection with *quality* is apparent.

* * *

Reference
[1] Anderson and Truter, *J. Textile Inst.*, **51**, T884 (1960).

Notes

Election of Fellows

At a meeting of Council held on 4th January 1961, the following were elected Fellows of the Society—

James Harry France Hilton

Manchester; Works Dyehouse Superintendent, Clayton Aniline Co. Ltd

Walter Hargreaves Hindle

President, Fiber Development Consultants, New York, N.Y., U.S.A.

Geoffrey Pullan Pearson

Guiseley, near Leeds; Dyehouse Manager, James Smith & Sons (Cleaners) Ltd, Dewsbury

Council Meeting— 2nd November 1960

Among the matters discussed at the meeting of Council on 2nd November were—

MEDALS AND AWARDS— Awards of medals for 1960 were approved; details appeared in the *January* issue (p. 23).

BRISTOL SYMPOSIUM— The title of the symposium will be "Science and Craft in Both Textile and Non-textile Coloration". A detailed programme will be announced in the *Journal* as soon as possible.

HONORARY FELLOWSHIP— Council decided to recommend to the Annual General Meeting, to be held on 28th April 1961, that it be empowered to award Honorary Fellowships. Honorary Fellowship would differ from Honorary Membership in that it would primarily be awarded to non-members who had achieved eminence in industry, technology, science, general scholarship or education.

MEMBERS' SUBSCRIPTIONS ON RETIREMENT— Council decided to recommend to the A.G.M. that members who have paid subscriptions for at least 20 years and who retire at the age of 60 years or over may pay reduced subscriptions without forfeiting the right to describe themselves at Associates or Fellows, where appropriate.

Presentation of Medals and Diplomas

As announced in the *January* issue, Medals and Diplomas will be presented at a special ceremony to be held at the Victoria Hotel, Bridge Street, Bradford, on 1st March 1961. Afternoon tea will be provided at 4 p.m. and the presentation ceremony will begin at 4.45 p.m.

Pure and Applied Chemistry

This new journal has been founded to collect into one publication all the reports and papers prepared by the International Union of Pure and Applied Chemistry (IUPAC). In addition to IUPAC publications, the journal will also contain, when appropriate, reports of meetings and symposia held under the aegis of the International Council of Scientific Unions (ICSU).

The journal will be published at irregular intervals, four parts per volume. Each volume will contain approx. 500 pages, and the subscription price is £6 ($18.00) including postage. The publishers are Butterworths, 4 and 5 Bell Yard, London W.C.2.

Soviet Technology Digest

Pergamon Press Ltd published in December 1960 the first issue of this journal, which is to be issued monthly at an annual subscription rate of £10 ($30.00). Digests of articles appear under four headings: Design and Production; Metallurgy, Welding and Foundry Production; Instruments and Automation; and General. In each section there are abstracts of some 10 papers, followed by translated contents lists of a number of Russian and other east European journals. Details are available from Pergamon Press Ltd, Headington Hill Hall, Oxford, England, or 122 East 55th Street, New York 22, N.Y., U.S.A.

Society of Leather Trades' Chemists Symposium

The Society is holding a symposium in the Physical Chemistry Department, Lensfield Road, Cambridge, on 23rd and 24th March 1961. The subject is "The Technology of Dyeing Fibrous Materials with particular reference to Leather". Other substrates to be considered are textiles, paper, timber and gelatin. Details are obtainable from Mr. G. H. W. Humphreys, 3 The Grove, Radlett, Herts.

Conference on Materials Handling

The Second International Conference organised by the Institute of Materials Handling is to take place in Southport on 10th–12th May 1961. Construction, procurement, manufacture, and transport and distribution will be examined in relation to the materials handling problems in agriculture and food production, extractive (minerals) and chemical industries, and the heavy and light industries. Standardisation will also be discussed. Details are available from The Institute of Materials Handling, 32 Watling Street, London E.C.4.

Man-made Fibres in the Woollen and Worsted Industry

A series of lectures on this subject will take place in the Department of Textile Industries at the Bradford Institute of Technology on Monday evenings at 7.30 p.m. over the period 10th April to 15th May 1961. Lectures will be given on the uses of nylon, Terylene, Fibro, Tricel, Acrilan, and Courtelle in the woollen and worsted industry.

Further details and forms of application may be obtained from the Registrar of the Institute.

Textile Institute Conferences

The Textile Institute is to hold two conferences during 1961. The Annual Conference will be held at Harrogate on 15th–19th May on the subject "Bulked Yarns and other Modified Textiles". The Overseas Conference will be held at Scheveningen, Holland, on 7th–12th September, the subject being "Crease-resistance and Crease-recovery".

Laboratory Apparatus and Materials Exhibition

The second national Laboratory Apparatus and Materials Exhibition will be held in the Royal Horticultural Society's New Hall, Westminster, on 19th–22nd June 1961. Both British and foreign equipment will be on display.

International Union of Pure and Applied Chemistry

The XXIst International Conference of the International Union of Pure and Applied Chemistry will be held in Montreal on 2nd–5th August 1961, and the XVIIIth International Congress of Pure and Applied Chemistry will be held in Montreal on 6th–12th August 1961. Information about the scientific programme of the Congress, and the plenary and sessional lectures, may be obtained from the Secretary, Central Committee, XVIIIth International Congress of Pure and Applied Chemistry, National Research Council, Ottawa, Canada. Early application is advisable.

Hochveredlung 1961

The Swiss Association of Colour Chemists (SVCC) is to hold a symposium on textile finishing, under the title "Hochveredlung, 1961", on 12th–14th October 1961 at the Federal Technical University in Zurich. Some 20 papers will be presented on the finishing of cellulosic and synthetic fibres, including testing, evaluation, and market problems.

Perrotts (Nicol and Peyton) Ltd
250th Anniversary as London Shrinkers

This firm, the oldest clothworkers in London, is now celebrating the 250th anniversary of its foundation in 1711.

Death of Members

We regret to report the death of Mr. E. Brunner, Mr. T. Minshall, and Mr. D. S. Naylor.

Meetings of Council and Committees
January

Council— 4th

Date on Identification of Dyes on Textile Fibres— 6th

Colour Index Editorial Board— 13th

Bristol Symposium Technical Papers Sub-committee— 16th

Washing Fastness Subcommittee— 17th

Publications— 17th

Finance and General Purposes— 19th

International Relations— 25th

Review of Textile Progress— 26th

OBITUARY NOTICE

E. Elöd

Egon Elöd, Director of the Staatliches Institut für Textilchemie, Badenweiler, Germany, died on 13th November 1960, in his 70th year. He was well known through his many publications, more than 200 in number, and did valuable research work on many aspects of textile science, including the structure of cellulose, weighting of silk, dyeing of polyamide fibres, chemical finishing, problems of colloid chemistry, the theory of dyeing and many other related subjects.

Prof. Elöd was born in Hungary. After graduating in chemistry at the Technische Hochschule in Karlsruhe, he founded there an Institute for Textile and Leather Chemistry, of which he was Director for many years. After the Second World War he formed, with governmental help, the Staatliches Institut für Textilchemie in Badenweiler where, assisted by many colleagues, he was able to continue his studies in textile research and technology. Prof. Elöd, himself an excellent scientist, never lost sight of the practical aspects of research. He also acted as industrial consultant and his advice was widely sought. Only recently he returned from a visit to textile mills in Japan.

He was also a very good teacher and his Institute in Badenweiler attained a world-wide reputation. He was awarded the Gold Medal of the International Federation of Associations of Textile Chemists and Colourists and the "grosse Verdienstkreuz der deutschen Bundesrepublik", and was elected an Honorary Member of many associations. After the war he succeeded in reconstituting the German Association of Textile Chemists and Colourists, of which he was President until his death. In 1959 he visited London for the International Congress of the Federation of Associations of Textile Chemists and Colourists and took part in the discussions and deliberations.

Prof. Elöd remained youthful and active all his life and was keenly interested in his work and studies. He radiated enthusiasm and inspired everyone he met; he will be greatly missed.

A. F. KERTESS

New Books and Publications

Annual Reports on the Progress of Chemistry for 1959
Volume 56

Pp. 476. London: The Chemical Society, 1960. Price, 40s. 0d.

In this report, which is somewhat smaller than its predecessor, the five main sections of the latter are retained, and the first of them— *General and Physical Chemistry*— follows the previous pattern of specialised coverage, the topics having been chosen to fill in some of the gaps that were left last year. In the field of molecular structure, consideration is given to nuclear magnetic resonance, absorption spectra, and the stability of complex ions, with relevant thermodynamics. Developments in electrochemistry are continued from the 1958 review and the main topic is the hydration of ions.

Under *Inorganic Chemistry* the elements are classified as before on the basis of the long form of the Periodic Table. Many subjects are discussed here, but *Organic Chemistry* remains by far the largest section. Much progress is reported in the assignment of absolute configurations, and conformational, mechanistic, and theoretical approaches to this problem are discussed. Of great interest and promise is a procedure for the computation of molecular rotations from the polarisabilities of the components of asymmetric groups. A second example is now recorded of a compound (pentaerythritol tetramenthyl ester) which owes its optical inactivity to a four-fold alternating axis of symmetry. The importance of entropy in determining equilibria and rates of isomerisation is emphasised in a number of investigations.

Zero-order nitration has been extended to the *N*-nitration of *N*-methyl-2,4,6-trinitroaniline and to the *O*-nitration of methyl alcohol, 4-nitrobenzyl alcohol, ethylene glycol, trimethylene glycol, and glycerol, and both processes are interpreted as a slow rate-determining formation of NO_2^+ followed by a fast reaction with the substrate. The difference in isomer proportions sometimes observed between nitration in acetic anhydride and in sulphuric acid, is ascribed to the increased electrostatic interaction between the electrophilic reagent and the molecular dipole of the substrate owing to the lower dielectric constant of acetic anhydride. Recently, the orientation of nitration has been re-examined for substitution in toluene, *o*- and *p*-nitrotoluene, ethyl benzoate, and benzonitrile. Direct introduction of the diazonium group has been achieved in high yield for simple phenols and phenolsulphonic acids, but the reaction when applied to hydroxy-acids involves decarboxylation; nitrosation is invariably the initial step in these reactions. The dealkylation sometimes observed in the diazo-coupling of phenol ethers is now known to occur after the coupling. A new biosynthetic theory has been proposed which challenges the view that alkaloids arise in the main from amino-acids. Nitrogen-containing sugars are reviewed.

Sections on *Biological Chemistry* and *Analytical Chemistry* complete the book. Special reference is made to the study of accuracy in titrimetric procedure, to the extended field of usefulness of zinc dithiol, and to an important micro-method for the determination of molecular weights on < 5 mg of sample with an error of $< 2\%$.

The book gives an impressive and invaluable record of the progress of chemistry during 1959.

H. H. Hodgson

The Chemistry of Natural Products
Volume V— The Carbohydrates

By S. F. Dyke. Pp. x + 232. New York and London: Interscience Publishers. 1960. Price, 36s. 0d.

This book is the fifth of a series dealing with natural products, and contains ten chapters dealing with general reactions, configuration, ring structures and derivatives of monosaccharides, less common naturally occurring sugars, plant glycosides, oligosaccharides, polysaccharides, and carbohydrate metabolism. The general object of the series is to provide undergraduate students with inexpensive sources of information intermediate in scope between the general textbook and the comprehensive monograph. "Vital information" on degradative and synthetic work is presented "shorn of all frills of unnecessary discussion".

The result, in this instance, is a set of lecture notes, clearly written and up-to-date, with honest acknowledgment of indebtedness to other authors, where appropriate, but the price is not particularly cheap for a short book with many blank and partly blank pages. The latter arise from the policy of reserving all the right-hand pages for handwritten formulae which, incidentally, are not very easy to read.

The book may prove useful for the purpose of passing examinations, but its educational value must be doubted. The process of condensation has been carried too far, resulting in an occasional lack of clarity, especially in the section on conformational analysis— a subject which demands adequate treatment if it is to be understood by the student. Too much background information is missing, and in many instances the natural origin of the substances discussed is not mentioned. It might seem superfluous to explain that sucrose is ordinary cane or beet sugar, but it would have been simpler than describing it as "a very commonly occurring sugar".

There are several errors, ranging from the relatively trivial, e.g. meso- for meta-saccharinic acid (p. 54), to the more serious. Hypoiodite (p. 8) may sometimes oxidise primary and secondary hydroxyl groups through side reactions, but that is not its main reaction with the sugars. As an α-hydroxyaldehyde, the branched sugar cordycepose (p. 96) should normally be oxidised by periodate, but it is said not to be, and a puzzling

deduction follows. Reference to the original work reveals that it is cordycepin (9-cordyceposido-adenine) which is not oxidised, and the structure assigned to cordycepose hinges on this fact. The enantiomorph of 2,3,5-tri-O-methyl-D-arabono-1,4-lactone (XLVIII; p. 147) is derived from 2,3,5-tri-O-methyl-L-arabofuranose and not from 2,3,4-tri-O-methyl-L-arabopyranose (XXXVII; p. 145).

It may seem unfair to single out the section on cellulose, but this is a review for dyers and colourists, and cellulose is of outstanding interest to them. It is no surprise to find that there is little mention of anything except the structural work of Haworth and others. Cellulose chemistry, as detailed in Ott's three volumes, finds no reflection here, though a few lines devoted to the charac-teristic topochemistry of this exceptionally important polysaccharide would not have been out of place. Symptomatic of this unawareness of ordinary cellulose chemistry is the space devoted to Haworth's alleged loop structure for cellulose, produced at a time when polymer chemists were already alive to the connection between chain length in linear macromolecules and fibre-forming properties. It is odd to read in 1960 that "the loop structure must now be abandoned" but, in fact, Haworth did not propose such a structure for native cellulose in 1939. He postulated the loops to explain the results of methylation experiments and it is clear that he regarded them as artifacts.

F. S. H. HEAD

Acrylic Resins

By Milton B. Horn. Pp. vii + 184. New York and London: Reinhold Publishing Corporation and Chapman & Hall Ltd. 1960. Price, 36s. 0d.

This book is another in the Reinhold series of small volumes, each of which deals with the manu-facture and technology of a specific type of resin. In this case the book has obviously been written by someone more interested in the practical use of the resins than in the fundamental theoretical aspects.

Very little space is devoted to the chemistry of the acrylic monomers and polymers, and the treat-ment is of an elementary and casual nature. Thus, for example, the description of the original synthesis of methyl methacrylate by the acetone–cyanhydrin process leaves the reader in some doubt as to whether or not this is the present commercial method. The inclusion of another paragraph would possibly have made the matter clearer, and it should have been stated that the end-product in the formulated reaction scheme is methyl meth-acrylate and not methacrylic acid. Inclusion of reaction formulae in the short paragraph on chemical reactions of acrylic monomers would also be extremely useful.

Technical applications, on the other hand, are presented in a very thorough and readable manner. Chapters deal with the manufacture, properties and fabrication of cast acrylics, moulding powders, emulsions, and solutions, respectively. In all cases the accounts are precise and interesting. Exact details are given for carrying out polymerisations,

both on a laboratory and on the manufacturing scale, but again no chemical reactions are detailed. Extremely precise details are often given, for example, on the best methods for cutting and machining cast acrylic materials, showing a first-hand knowledge of the manufacturing processes involved.

Many interesting applications of acrylic resins are described, e.g. their use in floor polishes, viscostatic oils, paints, and adhesives. From the point of view of the textile and dye chemist the amount of information on acrylic fibres is negligible. There is, however, a small section on the application of acrylic emulsions to textile fibres to improve their properties. To the fibre chemist this is tantalising in its brevity as compared to the amount of material dealing with other topics.

An appendix is included which suggests further general reading; this is never as useful as precise literature references, which are not included in the book. The book is well printed and contains few errors; the inevitable quinquevalent carbon atom on p. 18 and the misprinting of monomer for polymer on p. 46 are easily forgiven in such a pleasantly readable account.

R. S. ASQUITH

An Introduction to Practical Infrared Spectroscopy

By A. D. Cross. Pp. vii + 80 + 1 Table. London: Butterworths Scientific Publications. 1960. Price, 17s. 6d.

Of the many physical techniques that have been adapted since 1945 to the needs of organic chemists in solving problems of identification, analysis and structural diagnosis, infrared spectroscopy is perhaps the most widely applied. The recent development of relatively cheap, simplified spectrometers has further encouraged chemists to use the technique on a day-to-day basis. The time is therefore most opportune for the appearance of a small book written primarily for those with little spectroscopic background who wish to apply the method to their problems.

Dr. Cross deals with both determination and interpretation of infrared spectra. Part I of the book devotes roughly equal space to practical techniques and to interpretation. The practical side is admirably dealt with in sections covering the construction and operation of instruments, methods of sample preparation, and the use of solvents. The remainder of Part I deals broadly with interpretation of spectra, the material being rather arbitrarily divided into sections headed Elementary Theory, Uses of Infrared Spectroscopy, Quantitative Analysis, Hydrogen Bonding, and Interpretation of a Spectrum. On the whole, the treatment seems rather less satisfactory than is the practical part. It is, of course, easy to criticise on the grounds of omission a book where the author has probably chosen deliberately to be brief in order to keep down the price. However, some mention should have been made, while discussing the identification of unknowns, of the various collections of reference spectra now available. Also, in discussing the interpretation of an unknown

spectrum, a clearer statement might have been made of the spectral regions where one expects bands due to overtones, hydrogenic stretching modes, skeletal frequencies, etc. The section on quantitative analysis fails to stress the basic principles, and would have been improved by an illustrative example.

Part II consists mainly of 24 pages of charts and tables, summarising data on characteristic frequencies of organic compounds. The tables give excellent coverage of the field and show many good features, such as indications of band strengths, and of the reliability of the correlations. Their value would have been increased by more frequent literature references, since one often wishes to examine the original sources of correlations. Abbreviations such as o.o.p. (out of plane) are used more than is necessary; in some cases there is room for the words to have been printed in full.

In conclusion, it must be stressed that, despite these minor criticisms, there is no doubt that the book will provide a most valuable introduction to the subject for large numbers of undergraduates, research students, and practising organic chemists who lack the spectroscopic background necessary to use effectively the standard works of Bellamy, and Jones and Sandorfy.

M. St. C. Flett

The Technique of Photomicrography

By D. F. Lawson. Pp. xvi + 256 + 82 half-tone pp. + 4 pp. colour plates. London: George Newnes Ltd. 1960. Price, 55s. 0d.

Recent developments in the optical system of the microscope, coupled with improved sources of illumination, have greatly increased the usefulness of the instrument in both routine and research work. Along with this wider use of microscopy has grown the need for the preparation of permanent records of micro-structures for reports, publications and filing systems. In this connection photomicrography plays a rôle of the highest importance. The book under review sets out to present a comprehensive survey of modern techniques in this field, the author, who is a photographer, writing from wide experience of this particular type of work.

After a useful chapter on photomacrography, which covers reproduction from actual size to ×20, an account is given of the components of the microscope (48 pp.). The importance of illumination in photomicrography is then considered and a good account is given of modern lamps. Techniques of darkfield illumination and the use of light filters are described, and a simple outline is given of the methods of polarisation, phase-contrast and interference microscopy. Reflection microscopy, and the use of infrared and ultraviolet radiation and X-rays are also considered in the chapter on Special Methods of Illumination. Various types of camera are described and further chapters are devoted to stereoscopic photomicrography, use of flash illumination, and colour photography. An excellent account is given of the techniques and

theoretical basis of plate and print processing. In the final chapter there is a general outline of mounting and staining methods. Readers of the *Journal* who are primarily interested in the application of microscopy to the study of fibrous materials would need to supplement the account given in this chapter by reference to more specialised works. The book ends with a glossary of terms and a useful bibliography.

The book is well printed on good-quality paper and an outstanding feature is the number and variety of the illustrations. More than 100 line drawings are incorporated in the text, and over 150 photomicrographs and photomacrographs are reproduced in monochrome and in colour. The examples are drawn from a wide range of chemical and biological investigations. Some minor errors were noted, e.g. invention of the compound microscope is generally attributed to Jansen and not to Galileo (p. 1). An arithmetical error appears to have been made in using the magnification formula (p. 8), and a spelling mistake (Siedentopf) occurs on p. 102. These are small points, however, which in no way detract from the over-all merit of the book. The author gives a most valuable account of the equipment and operations of photomicrography, and the work is heartily recommended to all who are interested in this important field.

J. L. Stoves

Rapid Statistical Calculations

By M. H. Quenouille. Pp. xv + 72 + ix. London: Charles Griffin & Co. Ltd. 1959. Price, 10s. 0d.

This is a collection of easy methods of estimating from numerical data their mean values and spread, confidence limits, the significance of differences between them, goodness of fit, and degree of association or regression. Most of the methods outlined are independent of any assumed distribution of the results. With each method an estimate is given of its efficiency and relative rapidity. Each is fully described algebraically on one page with a numerical example of its working-out on the facing page, so that it is quite clear how the numerical operations are to be carried out. In all, 35 tests are given, many of which are novel and have been extracted from a wide variety of statistical journals not readily available to the ordinary user of statistical tests. This is the main value of the present booklet— it really is pocket-sized (4 in. × 6 in.)— the price also being within reach of anyone's pocket.

The recommended computations are rapid but, as the author says, a quick method ceases to be quick when much time is wasted looking it up and finding whether it is appropriate to the problem in hand. For this reason the book is invaluable and can be highly recommended.

Readers who are apt to become confused by small errors must be warned that the author's use of σ instead of s on pages 5, 6 and 7 probably results from overprecision or is a printer's error.

L. Peters

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952),*
and also, together with symbols and the periodicals abstracted, in the annual index

I— PLANT; MACHINERY; BUILDINGS

Hydroextractors, Drying Machines and Polymerisers
SVF Fachorgan, **15** (Oct 1960) 617–708
Descriptions, with photographs and line diagrams, of
available apparatus.   M.T.

PATENTS

Carbon Black (C.I. Pigment Black 6 and 7) Furnace
United Kingdom Chemicals   *BP* 855,802 (25 Mar 1957)
Describes a furnace and the method of introducing a
hydrocarbon gas, vapour or atomised liquid, and the gas
which reacts with it.   C.O.C.

Pelleting Carbon Black (C.I. Pigment Black 6 and 7)
Phillips Petroleum Co.   *BP* 855,086 (U.S.A. 26 Aug 1957)

Slubbing Dyeing Machine
Kammgarnspinnerei Kaiserlautern
BP 848,821 (Germany 22 Oct 1956)
The cover of a slubbing dyeing machine moves in
response to any change in volume of the slubbing during
dyeing. The pressure on the slubbing is kept constant by a
pressure member placed on the cover and loaded by
adjustable pressure.   C.O.C.

Maintaining Constant Tension in Web being Fed into
Machines
Maschinenfabrik Benninger
BP 846,712 (Switzerland 21 Nov 1955)
The web is looped successively over a series of rollers,
some or all of which are driven. Each driven roller has
independent driving means having a flat speed–torque
curve and rotates at less than its rated speed. The power
transmitted by the drive is sufficient to overcome the
frictional resistance of the rolls. The pull necessary for
feeding the web is provided separately.   C.O.C.

Counteracting Tension Variations Present towards
either side of a Running Web
Cameron Machine Co. *BP* 846,820 (U.S.A. 12 June 1958)
Constant tension is maintained in a web being trans-
ferred from one roller to another by having a guide roller
directly subject to the tension of the web. This roller is
hydraulically supported or backed-up at both its ends, the
supporting or backing liquid at opposite ends of the roller
being sensitive to tension variations imposed by the web
toward both ends of the roller. The two bodies of liquid
are so contained and used in a hydraulic control system
that tension variations in the web toward either or both
ends of the roller control a brake working on the payout
roll from which the web is being unwound. This effects
compensation for the web-tension variations and restores
the desired tension to the web.   C.O.C.

Wet Processing of Cloth
Flaxall Products   *BP* 849,927 (11 July 1957)
A number of rollers are spaced out across the top and
bottom of the bath. The bottom rollers are held stationary
with respect to the bath. Cloth is guided by these rollers
up and down several times through the bath. The cloth is
kept under constant tension. The top rollers are mounted
on a carrier which reciprocates to and fro horizontally
while the cloth is passing through the bath.   C.O.C.

Machine for Washing Printed Cloth in Open Width
"S.T.S." Stamperia Tessuti Serici
BP 846,802 (Italy 9 May 1957)
Several series of rollers are arranged as concentric
polygons. At least one of the sets is contained in a tank
holding the detergent liquor and at least one of the sets is
situated outside the tank so that as the cloth passes around
the rollers it proceeds in a spiral path into and out of the
tank. The cloth has the liquor sprayed on to it from nozzles
close to each non-immersed roller. Rotary brushes treat
the cloth at or towards the end of washing.   C.O.C.

Drying Machine for Cloth or Paper
Famatex   *BP* 849,633 (Germany 23 Jan 1957)
Method of arranging the nozzles with resulting simplified
construction of the machine and saving of space. C.O.C.

Drying Cloth in Fluidised Beds
British Rayon Research Association
BP 849,329 (18 Feb 1956)
The cloth is passed into and out of the bed through a
seal in the base of the container. This seal comprises
unfluidised particles of larger size than those forming the
fluid bed.   C.O.C.

Fluidised Bed Treatment of Textiles
British Rayon Research Association
BP 848,676 (7 Mar 1957)
Stresses and tension in the material passing through the
bed are minimised by having close to the travelling material
means to impede horizontal movement of the bed's
particles.

BP 848,677 (7 Mar 1957)
Improved sealing means which reduces tension imparted
to the material as it enters or leaves through the base of
the bed.   C.O.C.

Drying or Heating Textile Fabrics
F. Smith & Co. (Whitworth)   *BP* 850,859 (8 July 1958)
The bed of a fluidised bed machine is in two sections. In
one the particles are heated, in the other the fabric is
treated with hot particles brought to it by gravity.
         C.O.C.

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Mechanism of the Stability of Free Films (Foams) of
Surface-active Agents
B. V. Deryagin, A. S. Titievskaya, and V. K. L. Vybornovo
Kolloid zhur., **22** (July–Aug 1960) 398–402
The influence of electrolyte, pressure, and temperature
on the thickness of the film formed between two bubbles in
solutions of various surface-active agents, has been
studied. Increase in concentration of electrolyte in a
solution of a surface-active agent can either affect the
stability of the film or decrease its thickness to a limiting
value 110–140 Å, when it becomes very stable, i.e. it is not
affected by further increase in concentration of electrolyte
or temperature and is only slightly affected by pressure.
The phenomenon is common to a whole range of agents
and is obviously independent of such factors as surface
tension. It is explained by presence of thermodynamic
equilibrium between capillary attraction and repulsive
forces, i.e. spreading pressure.   L.S.L.

Fluorocarbon Finishes and their Effect on Dyes
AATCC, Rhode Island Section
Amer. Dyestuff Rep., **49** (31 Oct 1960)
P 818, P 823, P 827
Fluorocarbons vary widely in their compatibility with
other finishing agents. As a class, thermosetting resins and
methylol stearamide water-repellent agents tend to
separate out but can be made compatible by adding a
surfactant. Water-repellent agents in general are com-
patible with fluorocarbons, but thermoplastic resins and
softeners vary even among similar chemical types. Oil-
and water-repellency are affected to varying degrees by
incorporation of other finishing agents with fluorocarbons.
Some water-repellent agents have synergistic effects upon
oil- and water-repellency. Fluorocarbons had no significant
effect upon the hue of the dyes tested and the dyes had no
appreciable effect upon oil- and water-repellency.
         C.O.C.

Cleavage of the Silicon–Silicon Bond by Dilute Acids
A. W. P. Jarvie and H. Gilman
Chem. and Ind., **41** (8 Oct 1960) 1271–1272
Details of the hydrolysis of 1,4-dichloro-octaphenyl-
tetrasilane (I) are given in which a small amount of
cleavage of the Si–Si bond occurs, and a 20% yield of
sym-tetraphenyldisilane (II) is formed. Reaction steps
appear to be initial formation of 1,4-dihydroxy-octa-
phenyltetrasilane, addition of a proton to one of the OH

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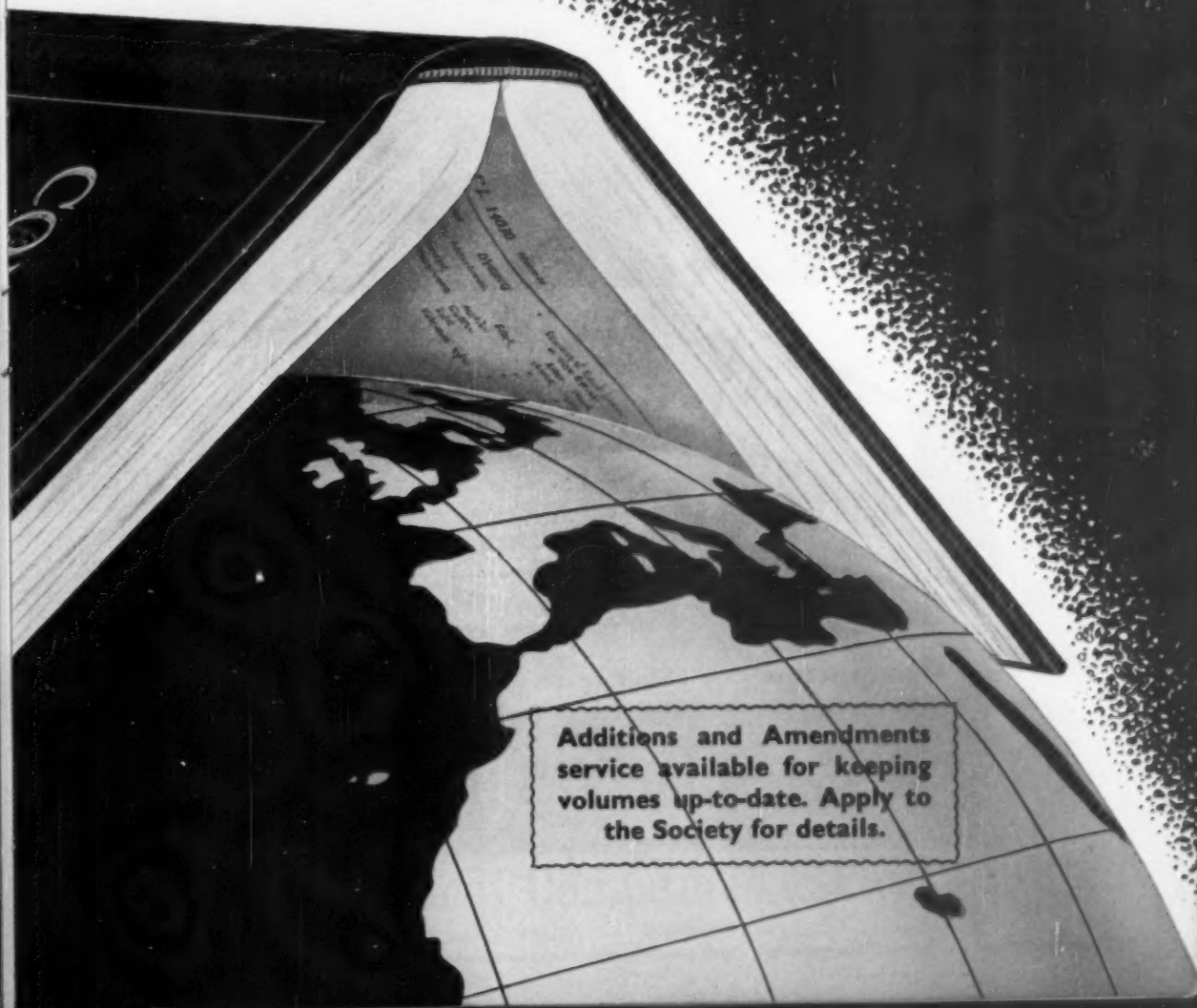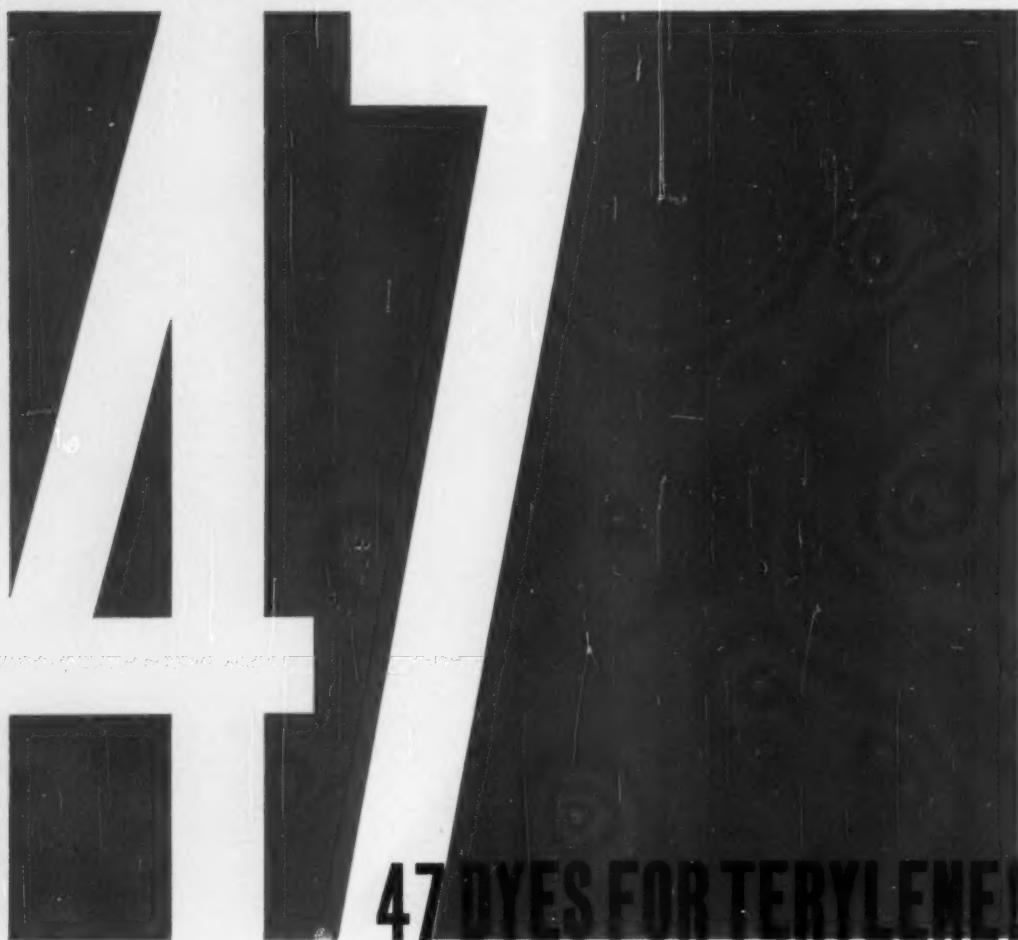
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United Kingdom
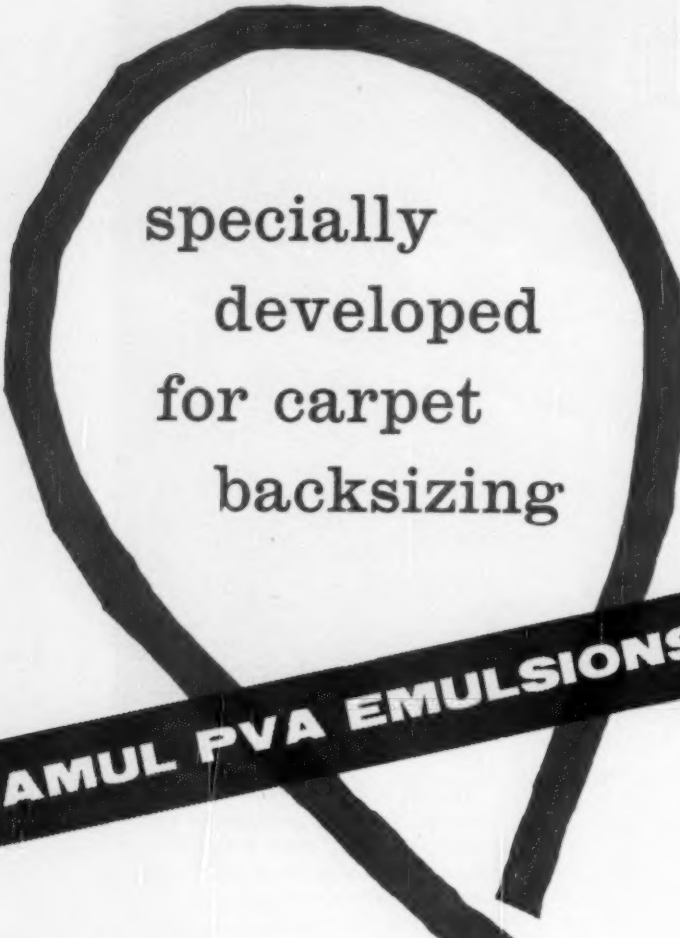
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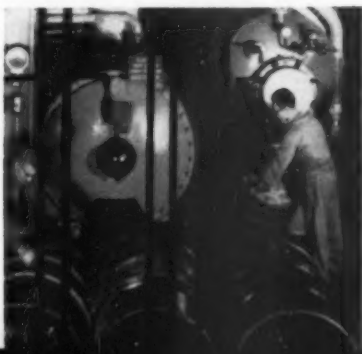
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groups, making the adjacent Si atom very susceptible to nucleophilic reagents, with subsequent attack by H_2O causing cleavage of the Si–Si bond and formation of a Si–H linkage, and repetition of the process at the other OH group to afford II; no diphenylsilanediol was isolated. When hydrolysis of I was cond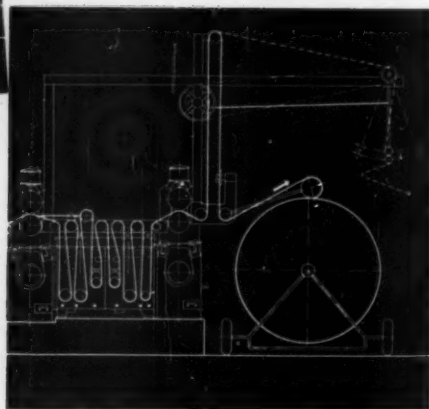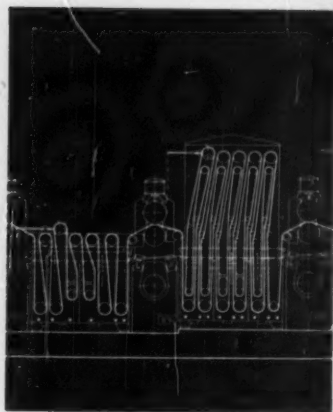ucted with 1 ml conc. HCl present, the yield of II was only 5%, showing the initial hydrolysis not to be acid catalysed. Further, it was found that the chromatography on alumina used for the isolation of II could only account for a small amount of cleavage. Hydrolysis of 1,6-dibromodecaphenylhexasilane under identical conditions gave a 56% yield of 1,6-dihydroxy-decaphenylhexasilane, while 1,4-dibromo-octaphenyltetrasilane afforded a 79% yield of octaphenylcyclotetrasilanoxide. H.H.H.

PATENTS

Sequestering Composition
Union Starch & Refining Co.
BP 852,958 (U.S.A. 7 Aug 1956)
An aqueous solution of a starch hydrolysis product having dextrose equivalent 30–90 has its aldehyde and keto groups carboxylated by the cyano reaction, followed by hydrolysis. The product has good sequestration properties for Ca, Mg, and Fe salts and also a strong dispersing power. C.O.C.

Nitrogenous Starch Ethers
Corn Products Co. *BP* 854,161 (13 Dec 1956)
Ungelatinised nitrogenous starch ethers in unswollen granular form are obtained by treating starch in presence of a strong alkali and a solvent with compounds of formula—

$$R^2 \cdot NHR^1 \text{ or } R^2 \overset{+}{N} R^3 R^4 R^5$$
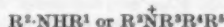
(R^1 = subst. or unsubst. Alk, cycloalkyl, alkenyl, Ar or aralkyl; R^2 = 2,3-epoxypropyl or 3-halogeno-2-hydroxypropyl; R^3, R^4, and R^5 = same or different subst. or unsubst. Alk, alkenyl, Ar or aralkyl, any two of them may form a ring but if all three are the same then each should be of < 5 C) followed by treating the resulting amine with an epihalogenohydrin. The products gelatinise in hot water to yield viscous pastes which do not set on standing. They are used as flocculating agents for anionic colloids, and as sizes and emulsifying agents. C.O.C.

Moth- and Rot-proofing Agents
FBy *BP* 854,956 (Germany 8 Dec 1956)
Compounds of formulae—
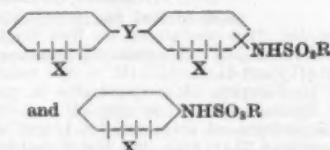
(X = same or different H, Cl or CF$_3$, at least one being CF$_3$; R = chloroaryl, chloroalkyl, chloroaralkyl or chlorocycloalkyl; Y = diphenyl linkage, O, S, SO, SO$_2$ or CH$_2$), e.g. 4'-chloro-4-trifluoromethyl-2-chloromethanesulphonylamino-1,1'-diphenyl ether, give keratin much greater protection against textile pests, fungi and bacteria than do the products of *BP* 738,758 (J.S.D.C., **72** (1956) 30). C.O.C.

9-Oxa-9,10-dihydrophenanthrene-10-one: Protecting Material Against the Effects of Light
United States Steel Corpn.
BP 851,649 (U.S.A. 4 Dec 1957)
Title cpd. gives good protection to coloured or uncoloured fibrous materials, paints, plastics, etc. against fading or deterioration caused by exposure to light. C.O.C.

Silicone Water-repellent Compositions
General Electric Co. *BP* 849,111 (U.S.A. 22 Nov 1955)
A composition having improved initial spray ratings and which gives a water-repellent finish fast to repeated dry cleaning comprises (1) a liquid methyl hydrogen polysiloxane (25–75% by wt.), (2) a curable, non-resinous, liquid product (75–25%) of hydrolysis of a mixture of methylchlorosilanes, and (3) stannous octoate, oleate or naphthenate in amount such that the Sn ion is ≪ 1% of the total weight of (1) and (2). The methylchlorosilane mixture consists essentially of dimethyldichlorosilane

(50–75%), trimethylchlorosilane (1–10), methyltrichlorosilane (10–35) and a methylchlorodisilane (0–10).
BP 847,426 (U.S.A. 13 May 1957)
A mixture of an orthotitanate, a methylpolysiloxane copolymer, a liquid polysiloxane and a wax is described which does not require heating to bring out optimum water-repellency of material treated with it. C.O.C.

Catalyst for Silicone Water-repellent Compositions
Monsanto Chemicals *BP* 847,414 (Belgium 15 Feb 1957)
The products obtained by dispersing 25–100% inorganic metal salt, e.g. TiCl$_4$, ZrCl$_3$, ZrCl$_2$ and CaCl$_2$, with an amine, e.g. monoisobutylamine, octylamine, cyclohexylamine or ethanolamine, are useful catalysts for curing aqueous silicone emulsions. C.O.C.

Synthetic Tanning Agents
BASF *BP* 855,571 (Germany 6 Apr 1957)
The title compounds are obtained by dispersing 25–100% of aldehyde–mono- or poly-hydric phenol condensates containing an insignificant number of SO$_3$H groups in the mixed condensates (I) of polynuclear aromatic sulphonic acids with aldehydes and halogenated phenols. They are used to give leathers of high fullness and a good greasy feel comparable with that obtained by vegetable tanning. I are the synthetic tanning agents of *BP* 747,675, *BP* 799,224 (J.S.D.C., **72** (1956) 358; **74** (1958) 705) and *GP* 695,374, and have great absorbing power for phenol resins, thus enabling resin dispersions to be prepared at a concentration not previously attainable.

BP 855,572 (Germany 8 Apr 1957)
Synthetic tanning agents of tannin ratio 85–90 and with similar properties to the above are obtained by further condensing mixed condensates of sulphonic acids of polynuclear aromatic hydrocarbons, halogen subst. phenols and aldehydes (especially those of *BP* 747,675 and 799,224 (see preceding abstract) in an acid medium, preferably at elevated temperature, with mono- or preferably poly-hydric phenols and aldehydes. They are obtained as pourable aqueous syrups, easily water-soluble, and convertible to powder by spray-drying. A.T.P.

Quaternary Salts of C-Vinylpyridine Polymers as Anti-static Agents for Sheet Materials and Textiles and as Wetting and Dispersing Agents
Kodak *BP* 852,923 (U.S.A. 3 Sept 1957)
  BP 855,028 (U.S.A. 3 Sept 1957)
A quaternary salt of a resinous C-vinylpyridine polymer of which 70% (by wt.) of the vinyl pyridine units are linearly recurring units of formula—
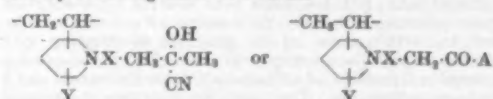
the remainder being of formula—

(Y = H or Alk of 1–4 C; X = Cl or Br; A = Alk of 1–3 C, phenyl, alkylphenyl, hydroxyphenyl, dihydroxyphenyl, halogenophenyl, aminophenyl, acetamidophenyl, alkoxy, vinyloxy, amino, alkylamino, anilino, dialkylamino or N-phenyl-N-alkylamino) are film forming. When applied to sheet materials, e.g. cellulose acetate film, they impart an excellent antistatic finish. They can also be applied to textiles or used as dispersing or wetting agents.
  C.O.C.

Solvents for Polyesters
Chemstrand Corpn. *BP* 854,032 (U.S.A. 9 Jan 1956)
α-Piperidone, caprolactam and compounds of formula—

(R = H or CH$_3$) or their mixtures with phenolic compounds, e.g. resorcinol, readily dissolve polyesters to yield non-gelling solutions. C.O.C.

Self-diffusion of Surface-active Agents in Nylon (VI p. 81)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Solubilities of Metal Chelates of α-Amino Acids
H. Irving and D. L. Pettit

Chem. and Ind., **41** (8 Oct 1960) 1268

The sharp decrease in the solubilities of chelate cupric complexes of α-amino acids with increasing length of alkyl chain has been attributed to steric hindrance to the co-ordination of water molecules. The much higher solubility of the cupric complex of cyclohexane-1-amino-1-carboxylic acid (I; $n = 3$) appears to support the above hypothesis since cyclisation prevents such hindrance, and it is now reported that the cupric complex of cyclopentane-1-amino-1-carboxylic acid (I; $n = 2$) is even more soluble. The small but regular increase in the solubility of the cupric complexes of (I) ($n = 2, 3,$ and 4) with increasing mol. wt. is held to be due to the "weighting

$$(CH_2)_n \quad C \begin{array}{c} CH_2 \diagdown NH_2 \\ \diagup \diagdown \\ CH_2 \diagup COOH \end{array}$$

(I)

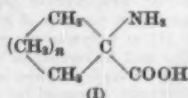effect" (cf. Feigl, *'Specific, Selective and Sensitive Reactions'*, 1949, New York: Academic Press Inc., p. 146 *et seq.*), and this is now supported by the solubilities of the corresponding 1 : 2-nickel complexes.   H.H.H.

The Structure of Double Diazonium Salts
L. A. Kazitsÿma, O. A. Reutov, and Z. F. Buchkovskiĭ

Izvestiya Akad. Nauk. SSSR, otdel. khim. nauk, No. 8 (Aug 1960) 1523

The formula of double salts of diazonium compounds and metal halides is generally accepted as $Ar–N^+ = N[MX_{n+1}]^-$, where the metal atom is not chemically attached to trivalent nitrogen. The evidence obtained by infrared and ultraviolet spectroscopy of certain complexes of cobalt and copper chlorides suggests that this is not so and that there is a chemical link between metal and trivalent nitrogen.   L.S.L.

Reactions of Diazonium Salts with Nucleophiles
E. S. Lewis and M. D. Johnson

VI— Reactions of *p*-Phenylene-bis-diazonium Ion with Water

J. Amer. Chem. Soc., **82** (20 Oct 1960) 5399–5407

The kinetics of the reactions of *p*-phenylene-bis-diazonium ions (tetrazotised *p*-phenylenediamine) in buffered soln., pH 2–4, have been studied by absorption spectrophotometry of the various species existing in soln. and, in certain cases, of the products of coupling with 2-aminonaphthalene-6-sulphonic acid. The ion showed a reversible formation of a mono-*anti*-diazo-hydroxide and a mono-*anti*-diazotate. The mono-*syn*-diazotate is assumed to be rapidly isomerised. Although spectrophotometrically undetected, the mono-*syn*-diazohydroxide was shown to give the *p*-hydroxybenzenediazonium ion, probably formed through a cyclic transition state—

$$N{=}N{=}\underset{}{\overset{+}{\bigcirc}}\underset{N'}{\overset{\overset{\displaystyle H}{\underset{O}{|}}}{N}}{}^+$$

Other theoretical possibilities may contribute to a minor degree in the formation of *p*-hydroxybenzene-diazonium ion. A scheme is discussed in which two substances, interconverted reversibly, each yield a third substance by an irreversible path. The scheme fits, within satisfactory precision, the case of the tetrazonium salt hydrolysis.

VII— *p*-Phenylene-bis-diazonium Ion

Ibid., 5408–5410

In acidic aq. soln., tetrazotised *p*-phenylenediamine reacted with chloride, bromide, thiocyanate or azide ions to give corresponding *p*-substituted benzenediazonium ions at rates greater than that of any reaction of the second diazonium group. Mechanism of the substitution reactions is believed to involve transition states with bonding to carbon and to ω-nitrogen atom. The extent of the latter may be correlated with stability of the corresponding covalent diazo compound; thus OH^- and N_3^- could be expected to retain bonding to nitrogen in transition state. In high concn., iodide ions gave *p*-di-iodobenzene with

tetrazotised *p*-phenylenediamine and at lower concn. the *p*-iodobenzenediazonium ion. At concn. low enough for rates to be measured, the *p*-hydroxybenzenediazonium ion was formed by a reaction assumed to involve dissolved oxygen.   F.J.

Change in Colour of Vat Dyes on Soaping
L. M. Golomb; J. Wegmann

J.S.D.C., **76** (Dec 1960) 679–680

Bitolyl Derivatives as Azo Dyes
E. Angeletti

Boll. sci. fac. chem. ind. Bologna, **18** (1960) 27–28
Chem. Abs., **54** (25 Sept 1960) 18961

6-Substituted derivatives of 2,2'-dimethyl-6'-amino biphenyl (1) were coupled with β-naphthol to determine the effect of *ortho* substitution in (I) compared with that in a benzene ring. The 6-substituent, colour, % yield and colour on wool were: NO_2, orange-red, 65, dark apricot; 2-hydroxy-1-naphthylazo, scarlet, 70, beige; Cl, deep red, 72, light apricot; Br, deep red, 50, orange; I, deep red, 48, rosy beige. All dyeings were fast to water for 16 h at 20°C, but not as fast to washing. The NO_2 derivative was the least and the I derivative the most fast when treated for 30 min in a 5% soap and 0·2% Na_2CO_3 solution at 60°C. Auxochromic character increased from the Cl to the I derivative with corresponding increase in light fastness.
                C.O.C.

Relationship of Structure of Benzanilide Dyes to their Properties. I— Influence of Some Structural Factors of 4,4'-Diaminobenzamide-derived Dyes on their Hue and Direct Dyeing Properties
B. M. Krasovitskiĭ, D. G. Pereyaslova and T. V. Oleĭnik

Uchenye Zapiski Khar'kov. Gosudarst. Univ. im. A. M. Gor'kogo, **76**, *Trudy Khim. Fak. i Nauch.-Issledovatel. Inst. Khim.*, (15) (1956) 129–133
Chem. Abs., **54** (25 Sept 1960) 18963

The number of azo groups and their distribution in relation to the amide groups of benzanilide-derived dyes greatly influences their direct dyeing properties. Dyes derived from 4,4'-diaminobenzanilide are markedly different, both in intensity of colour and in direct dyeing properties, from those derived from 3,3'-, 3,4'-, and 3',4-diaminobenzanilide, and from those from 3-, 3'-, 4-, and 4'-aminobenzanilide.   C.O.C.

Constitution of Chromium Complexes of Azo Dyes
E. P. Fokin and N. N. Karandasheva

Zhur. Vsesoyuz. Khim. Obshchestva im. D. I. Mendeleeva, **5** (1960) 235–236
Chem. Abs., **54** (10 Sept 1960) 17891

Dihydroxyazo dyes containing no free SO_3H groups, when chromed with NaCr salicylate (I), form complexes of type $RCrY$ (II) and R_2Cr (III) (R = dye residue; Y = residue of I). Complex II predominates in presence of excess I. Boiling aq. 0·01-M dye A and 0·02-M (I) produced a mixture of complexes A-1 and A-2. The former eluted from Al_2O_3 with 50% NaOH had R : Cr : Y = 1·06 : 1·0 : 0·75 (approaching that of II). Complex A-2, eluted with methanol, had a ratio of 2·06 : 1 : 0 (approaching that of III). Similar treatment of the isomer of A, dye B, gave a mixture of complexes, which on chromatographic separation gave complexes B-1 and B-2 with ratios of R : Cr : Y of 2 : 1 : 2 and 2·93 : 1 : 0, respectively. Complex B-1 predominated in presence of excess I. Complex B-1 was unstable and changed into B-2 on standing; conversion was accelerated by presence of traces of acid. B-2 was stable. Prolonged heating of 0·01-M B with 0·05-M Cr acetate in alkaline medium gave only the B-2 complex. Thus two new types of complexes were formed: R_3CrY_3 and R_3Cr. Dye A was prepared by coupling 2-aminophenol-5-sulphonamide with 1-(2-chlorophenyl)-3-methyl-5-pyrazole and dye B similarly, using diazotised 2-aminophenol-4-sulphonamide.   C.O.C.

Substitution of Halogen in Azo Compounds. XII— Effect of Different Halogens
M. A. Andreeva and B. I. Stepanov

Zhur. obshch. khim., **30** (Aug 1960) 2768–2771

From the reaction of 2-fluoro-, 2-chloro-, 2-bromo- and 2-iodo-benzene-(1-azo-1')-naphth-2-ols with sodium methoxide in presence of cupric acetate, ease of replacement of halogen by the alkoxy group is in the order: $F \ll Cl < Br < I$. Practically no substitution occurs with F even on heating for 8 h at 100°C, whilst Br and I are quantitatively replaced after 1 h at 30°C.   G.J.K.

Direct Disazo Dyes— Oxadiazole and Thiadiazole Derivatives. II— Comparative Investigation of Isomeric Disazo Dyes— Derivatives of Thiadiazole
B. M. Krasovitskiĭ, R. M. Matskevich, N. S. Dokunikhin, and N. A. Trubitsȳna
Zhur. obshch. khim., **30** (Aug 1960) 2608–2613

Thiadiazole disazo dyes of formula—

$$R-N=N-\underset{(I)}{\underbrace{}}-N=N-R$$
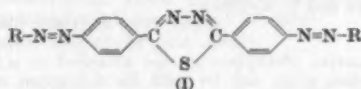
(R = Chicago or H acid) have been synthesised and their affinities for cotton investigated. In consequence of interruption of conjugation, isomeric dyes having the –N=N–R group in the *meta*-position show a hypsochromic effect and decrease in substantivity compared with I. Absorption peaks at low λ and poor affinity for cotton of the corresponding *ortho* isomers are attributed to steric factors.   G.J.K.

Chelated Azo Pigments derived from 2,4-Dihydroxy-quinoline
Y. Bansho, S. Suzuki, and I. Saito
Repts. Govt. Chem. Industr. Res. Inst., Tokyo,
55 (Aug 1960) 271–276

2,4-Dihydroxyquinoline was prepared by fusing sodium acetanthranilate (1 mol) with sodamide (6·2 mol) in a mixture of sodium and potassium hydroxides at 180–190°C. Several amines (nitroanilines, *p*-chloroaniline, *p*-toluidine, 3,3′-dichlorobenzidine, etc.) were diazotised and coupled with the 2,4-dihydroxyquinoline. Chelated pigments were then obtained by treating the products with Co, Ni, and Cu complex salts. Useful pigments were obtained with the Ni complex. The fastness to light, heat, and organic solvents of the chelated azo pigments were much higher than the fastness of the unchelated pigments.   M.T.

Polymethin Dyes. VI— Azacyanomethins
M. S. Strell and K. Rost   *Chem. Ber.*, **90** (1957) 1905
Chem. Abs., **54** (10 Aug 1960) 15936

A new series of dyes resembling cyanomethin dyes but containing azo bridges was synthesised. Thus, NC·CH₂Cl:NCl:CHCN (from NC·CH₂CONH₂ and POCl₃) is condensed with a wide range of aldehydes, e.g. *p*-(CH₃)₂N·C₆H₄·CH:CH·CHO, and 3-benzylglutaconic dialdehyde bis-(*N*-methylanilide) hydrobromide. λ_{max} are given in many cases.   A.T.P.

Dyes Containing the Indole Ring
J. R. Majer

I— Trinuclear Pentamethin Cyanines
Tetrahedron, **9** (1960), 106–110
*Chem. Abs.*, **54** (25 Sept 1960) 18468

Indole trimethincyanines condensed with homo- and hetero-cyclic aldehydes give a series of trinuclear dyes. Thus, a boiling acetic acid solution of 3-isopropylidene-2-methylindolenine sulphate treated with 2-phenylindole in boiling HC(OC₂H₅)₃ gives 3-(2-methylindole)-3′-(2-phenyl-indole)-α-methyltrimethincyanine sulphate. This, refluxed in 1 : 1 acetic acid–acetic anhydride with indole-3-carbox-aldehyde gives 3-(2-phenylindole)-3′-indole-γ-3″-(2-methylindole) pentamethincyanine sulphate.

II— Trinuclear Trimethincyanines
Ibid., 111–115
Chem. Abs., **54** (25 Sept 1960) 18469

Indoles containing a free β-position, when condensed with aliphatic acid chlorides and anhydrides, give sub-stituted di-indolylmethenes (I).

$$\text{(I)}$$
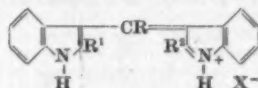
Thus, 2-methylindole yields products with C₂H₅·COCl (R = C₂H₅, R¹ = R² = CH₃) (II), C₆H₅·CH₂·COCl (R = C₆H₄CH₂, R¹ = R² = CH₃) (III), CH₃COCl (R = R¹ = R² = CH₃) (IV), (CH₂COCl)₂, to give αα′-ethylene bis-3-(2,2′-dimethyldi-indolylmethene)hydrochloride (V). I containing active CH₂ groups were then condensed with homo- and hetero-cyclic aldehydes, e.g. *p*-dimethylamino-benzaldehyde (VI), 2-methyl-3-indolecarboxaldehyde, to yield intensely coloured trinuclear cyanine dyes. Thus,

VI and II refluxed in acetic acid–acetic anhydride give dark blue needles of 3-(2-methylindole)-1′-(4-dimethyl-aminobenzene)-α-3″-(2-methylindole)-β-methyltrimethin-cyanine chloride. The dyes derived from VI vary consider-ably in their stability. Those from II and III are very rapidly destroyed in hot acetic anhydride, in contrast to the stable dyes from IV and V.   A.T.P.

p-Dialkylaminostyryl Dyes derived from 5-Aryl-aminothiadiazoles
P. B. Tripathy and M. K. Rout
J. Indian Chem. Soc., **37** (July 1960) 415–419

2 - *p* - Dimethylaminostyryl - 5 - phenylamino - 1,3,4 - thiadiazole (I) yields two mono-methiodides identical with the condensation products of (*a*) 5-phenylamino-2,3-dimethyl-1,3,4-thiadiazolium iodide (II) and *p*-dimethyl-aminobenzaldehyde (red) and (*b*) the 2-methyl thiadiazole and the methiodide of *p*-dimethylaminobenzaldehyde (colourless). A number of condensation products similar to (*a*) have been prepared from *p*-dimethyl- and *p*-diethyl-aminobenzaldehyde and (II) bearing substituents *o*-CH₃, *p*-CH₃, *p*-OC₂H₅, *p*-OCH₃ and *p*-Br. These dyes are held to be more basic than the corresponding quinoline and benzothiazole derivatives. Some spectral data are given.   A.J.

Phenazinimines: a Possible Explanation of Anomalies associated with Neutral Red (C.I. 50040)
D. L. Vivian   *Nature*, **188** (26 Nov 1960) 746–747

Differences in m.p., colour with conc. H₂SO₄, solubility in ether and fluorescence of the solution under ultraviolet radiation were observed between the purified base of the commercial dye and that prepared by the Vivian "unambiguous" method (*J. Org. Chem.*, **21** (1956) 565). If the dye obtained by the latter method is dissolved in sulphuric acid it acquires the same properties as the commercial dye. As separable isomers of 2-aminophen-azine do exist when the compound is further substituted by NH₂ or OH in 8-position, then, by analogy, there are probably two forms of Neutral Red base, viz.,—

$$\text{(H₃C)₂N} \qquad \text{and} \qquad \text{(H₃C)₂N}$$

C.O.C.
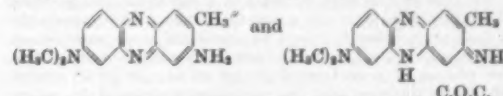
Azine Dyes, Derivatives of N-Methylbenz[cd]indo-line, for Cellulose Acetate
N. S. Dokunikhin and Ya. B. Shteĭnberg
Zhur. Vsesoyuz. Khim. Obshchestva im. I. D. Mendeleeva, **5** (1960) 110–111
Chem. Abs., **54** (25 Sept 1960) 18475

N-Methylbenz[cd]indoline-2-one oxime (I) and the corresponding hydrazine (II) could not be prepared directly from *N*-methylbenz[cd]indoline-2-one. The thione reacted with hydroxylamine (boiled 2 h in ethanol) to form I, m.p. 195·5–197°C, and with hydrazine hydrate to form II, m.p. 175–176°C. *N*-Methylthiobenz[cd]indolinium salts reacted with hydroxylamine (boiled 2 h in absolute alcohol in presence of triethylamine) to give I and with hydrazone hydrate to give a symmetrical red dye (III), λ_{max} 492, 528 mμ. Boiling II with *p*-dimethylaminobenzaldehyde in

$$\text{(III)}$$

$$\text{(IV)}$$
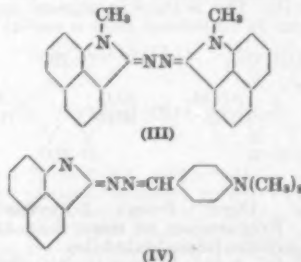
alcohol in presence of acetic acid yielded a yellow dye (IV), λ_{max} 446 mμ. II entered into oxidative azo coupling with phenols, amines and compounds containing an active CH₂ group. Azo coupling was especially active in presence of K₃Fe(CN)₆ in ammoniacal alcohol at room temperature. Condensing II with α-naphthol and 2-hydroxy-3-naphth-anilide, respectively, yielded the two red diazamero-cyanines—

λ_{max} 535 mμ λ_{max} 498, 532 mμ
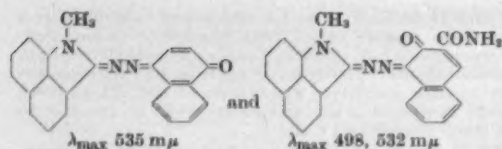
All four dyes whose formulae are given above dyed cellulose acetate.   C.O.C.

Products of the Nitration of Methylene Blue (C.I. 52015)

T. Urbański, K. Szyc-Lewańska, and P. Kalinowski
  Bull. acad. polon. sci., Sér. sci., Chim., Géol. et géograph., 7 (1959) 147–149 (*in English*)
      Chem. Abs., 54 (10 Sept 1960) 17403

The product obtained by Grehm and by the authors (*Chem. Abs.*, 53 (1959) 5269) was most probably 2,4-dinitro - 3 - (N - methylnitramino) - 7 - dimethylamino-phenothiazine *SS*-dioxide; and its hydrolysis product, identified previously as a phenol, was 2,4-dinitro-3-hydroxy-7-dimethylaminophenothiazine *SS*-dioxide.

                                                    C.O.C.

Excited States in Diketones and Quinones and the Photochemical Behaviour of Anthraquinone Dyes

F. Dörr   *Z. Elektrochem.*, 64 (1960) 580–582
      Chem. Abs., 54 (25 Oct 1960) 20474

The excited states reached by n-π transitions in diketones and quinones are discussed under the assumption that they represent diradicals. The chemical differences between radical electrons localised on O and delocalised in the π system are discussed. This concept is used to explain the photochemical properties of anthraquinone dyes and in particular the destruction of cotton in presence of some vat dyes.   C.O.C.

Anthraquinones of Teak (*Tectona Grandis* L.F.)

P. Rudman   *Chem. and Ind.*, 44 (29 Oct 1960) 1356–1357

Because of the high content of 2-methylanthraquinone which interferes in many separations, the crude extractives of teak with ether followed by methanol were partitioned 90 times in a Craig countercurrent extractor between the two phases of a methanol:petrol ether (40–70°C):water (60 : 60 : 5) mixture and the partitions examined by paper chromatography in methanol:chloroform (8:2) and in methanol-saturated heptane. By this means, 2-hydroxy-methyl-anthraquinone and anthraquinone-2-carboxylic acid were identified for the first time in natural products, and possibly also anthraquinone-2-aldehyde. In addition, teak has also the following extractives: 3-hydroxy-2-methylanthraquinone, lapachol, 2-methoxytoluene, 2-iodobenzoic acid, n-heptylamine, butyric acid, a *cis* 1,4-polyisoprene, tectol, and dehydrotectol.   H.H.H.

Structure of Namakochrome— II

T. Mukai
      Bull. Chem. Soc. Japan, 33 (Sept 1960) 1234–1235

Previous work (*ibid.*, 33 (1960) 453) to elucidate the structure of the new pigment namakochrome, isolated from *Polycheira rufescens*, is now continued, and the constitution established as 2-methoxy-3,6,7-trihydroxy-naphthazarin (I). This is the first pigment containing a methoxyl group to be isolated from a marine animal.
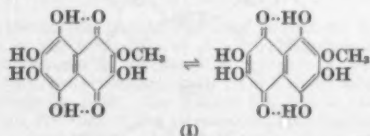
(I)

                                                    H.H.H.

Thioindigoid Dyes from 2-Arylimino-4-thi-azolidinone. Preparation of some 3-(2-Arylimino-4-oxo-5-thiazolidinylidene)oxindoles

R. P. Rao   *J. Sci. & Ind. Research* (India), 19B (1960) 29
      Chem. Abs., 54 (10 Sept 1960) 17376

The above oxindoles were prepared from isatin and 2-arylimino-4-thiazolidinone (I). Thus, arylthioureas were refluxed with chloroacetic acid in presence of Na acetate and ethanol to yield I. Then isatin and I (0·25 mole each), fused Na acetate (10 g), acetic anhydride (2 ml), and glacial acetic acid (40 ml) were refluxed at 150–160°C for 4–5 h. The mixture was poured into water,

filtered, and the filtrate washed with dil. acetic acid and ethanol. The following oxindoles were prepared (Ar of 2-arylimino group, colour): *o*-ethoxyphenyl, dark red; *p*-ethoxyphenyl, dark red; *p*-nitrophenyl, dark chocolate red; *o*-chlorophenyl, deep orange red; *m*-chlorophenyl, dark red; *p*-chlorophenyl, dark red.   C.O.C.
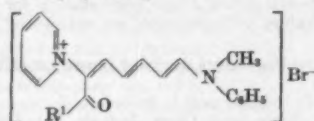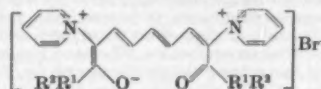
Cyanines— I

K. Dickoré and F. Kröhnke
            Chem. Ber., 93 (1960) 1068–1074
            Chem. Abs., 54 (25 Sept 1960) 18513

The reactive methylene groups attached to a hetero-cyclic onium atom can be used for formation of sym-metrical and unsymmetrical betaine cyanine. N-(p-Bromophenacyl)pyridinium bromide was treated with $CH_3 \cdot C_6H_5N(CH:CH)_2CHO$ (I) in acetic anhydride and then heated for 30 min on a water bath with ether; the precipitate was dissolved in hot $CHCl_3$, treated with C and evaporated slowly, yielding

(red when $R^1 = p\text{-}C_6H_5C_6H_4$). N-(p-Phenylphenacyl)-pyridinium bromide and I were treated similarly, and the ether precipitate was boiled with acetone, yielding

(blue when R^1 and $R^2 = p\text{-}BrC_6H_4$).   C.O.C.

Syntheses of ^{14}C-labelled Cyanine Dyes. II—Synthesis of *meso*Methyltrimethinthiacyanine by Use of Decomposition of the 2-Methylbenzothiazole Methiodide

K. Taki and Y. Hishiki
      Rikagaku Kenkyusho Hokoku, 35 (1959) 269–275
            Chem. Abs., 54 (10 Oct 1960) 20211

In the formation of Brooker's *meso*-methyltrimethin-thiacyanine dye, the C-CH$_3$ group in the centre of the dye molecule is provided by decomposition of some of the 2-methylbenzothiazole methiodide. When 2-methylbenz-oxazole methiodide is used with 2-methylbenzothiazole ethiodide to form this dye, the central C-CH$_3$ group is provided by both these compounds.   C.O.C.

Chemistry of Cyanine Dyes

I. K. Ushenko and L. I. Chovnik
   ## XV— Cyanine Dyes Containing Phthalimido Substituents
      Zhur. obshch. khim., 30 (Aug 1960) 2658–2664

Fusion of aminobenzothiazoles, aminobenzoxazoles, and aminoquinolines with phthalic anhydride yields corres-ponding phthalimido (R) deriv. Benzothiazolylphthal-imides are transformed into quaternary salts (Q8) and subsequently into cyanine dyes of formulae I and II—
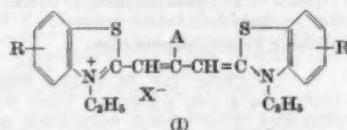
(I)

(A = H or C$_2$H$_5$; R in 6,6' or 5,5' position)
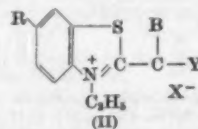
(II)

(Y = benzothiazolyl or CH— N(CH$_3$)$_2$; B = H or CH$_3$)

In I introduction of R (in either 5,5' or 6,6' position) has only a very slight bathochromic effect, whilst in II this effect is very pronounced. In II, replacement of H (in

position B) by CH_3 on the monomethinthiacyanine has a strong bathochromic effect, whilst in the case of the styryl dye the opposite displacement of the absorption max. occurs.

XVI— Biscyanines
Ibid., 2665–2669

The action of phosgene or dicarboxylic acid chlorides on benzene soln. of 2-methyl-6-amino- and 2-methyl-5-amino-benzothiazole yields 12 new symmetrical di-(3-methylbenzothiazolyl)-diamides of formula—

(R is –NH–CO–HN– or –NH–CO–$(CH_2)_n$–CO–HN– $n = 0$–4). The corresponding diquaternary salts are condensed with 2-acetanilidovinylbenzothiazole ethiodide to form bisthiacarbocyanines. Linking of two simple thiacarbocyanine residues by R produces a slight bathochromic effect. G.J.K.

Cyanine Dyes with Unsaturated Substituents. VII— Thiacyanines containing β-Cyanovinyl Radicals in the Benzothiazole Nucleus
I. K. Ushenko

Zhur. obshch. khim., 30 (Aug 1960) 2650–2657

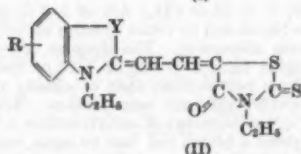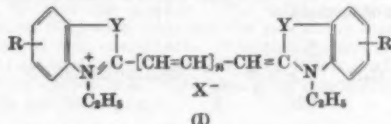Interaction of benzothiazolyldiazonium chlorides and acrylonitrile gives 2-methyl-5- and 2-methyl-6-(β-cyano-β-chloroethyl)-benzothiazoles. Elimination of hydrogen chloride yields the corresponding β-cyanovinyl bases, from the quaternary salts of which are obtained carbo- and thiacarbo-cyanines (I) and dimethinmesocyanines (II)—

(R = H; C_6H_5–CH=CH–; or NC–CH=CH–; Y = S or –CH=CH–; $n = 1$ or 2). Substitution of cyanovinyl group by styryl has little effect on absorption max. Formulae, physical const., and analytical data of 16 new cyanine dyes are tabulated. G.J.K.

Dichroism of Dyes in Stretched PVA Sheet IV— Absorption Spectra of Carbocyanines and Note on the Chemical Structures
Y. Tanizaki and H. Ono

Bull. Chem. Soc. Japan, 33 (Sept 1960) 1207–1214

The method of inspection discussed previously (*ibid.*, 33 (1960) 979) of dichroic curves observed at a high stretch ratio, is now applied to electronic spectra (above 220 mμ) afforded by 1,1′-diethyl-2,2′-cyanine, -dicarbocyanine, and -tricarbocyanine iodide, and -4,4′-cyanine iodide, respectively, in stretched polyvinyl alcohol sheets at a stretch ratio of ca. 6–10. The dichroic behaviour of the absorption bands may be interpreted by the transitions along the longitudinal axis of the mol. and by those, localised in the quinoline nuclei, in two directions at right angles. The second group absorptions corresponded to the overtones of the first group, and the systematic changes of band distances in these groups with variation of methin bond number are related with vibrational states. The state of strain in the various molecules is discussed.
H.H.H.

Dyes from Marigold as Substitute for Annatto (C.I. Natural Orange 4)
S. D. Shteĭnbok
Sostoyanie i Perspektivy Izuchen., Rastitel. Resursov S.S.S.R. (Moscow–Leningrad: Akad. Nauk. S.S.S.R.) *Sbornik*, (1958) 428–340; *Referat. Zhur. Khim.* (1959) Abstr. No. 44118
Chem. Abs., 54 (25 Sept 1960) 18963

The epidermis of the corollas of the marigold flowers, *Calendula officinalis*, contains a colorant consisting mostly of carotene (C.I. 75130) and lycopene (C.I. 75125). Two methods of extracting it have been developed: (1) the finely ground material is extracted with vegetable oil at 60–70°C, and (2) the material is extracted with alcohol at 50°C for 30 min, followed by vacuum evaporation of the extract. The oil-extracted pigment seems to be better for commercial purposes. Yield of pigment from the dry petals is 90%. (The above differs from the information given by previous workers, cf. C.I. Natural Yellow 27— C.O.C.)
C.O.C.

Reactive Dyes containing 2,4-Diamino-1,3,5-triazin-6-ylamino Groups
O. Manabe and H. Hiyama

Yûki Gôsei Kagaku Kyôkaishi, 18 (1960) 395–400
Chem. Abs., 54 (10 Sept 1960) 17889

An account of the synthesis and properties of dyes containing the above groups. J-acid (23·9 g) and Na_2CO_3 (5·3 g) in water (200 cm³) had acetic anhydride (14·7 g) stirred in at 20°C. The mixture was stirred for 30 min at 35°C, Na_2CO_3 (14·5 g) added, heated at 95°C for 15 min and Na_2CO_3 (16 g) added to yield a coupling solution (I). Sulphanilic acid (0·98 mole) was diazotised and I added at 20°C, the mixture was stirred for 2 h, heated at 95°C for 3 h with NaOH (20 g), neutralised with HCl, salted out with NaCl and the resultant mass dissolved in water (300 cm³). The solution was cooled with ice, cyanuric chloride (9·7 g) in acetone (70 cm³) added, an aq. soln. of Na_2CO_3 (2·7 g) added gradually, stirred for 1 h and salted with NaCl. The mixture was filtered, the resultant paste dissolved in 10% NH_4OH (200 cm³), heated in an autoclave at 40°C for 3 h, then at 100°C for 2 h, neutralised with HCl, salted out with NaCl (20 g) and the precipitate washed with 20% brine to yield 6-(2,4-diamino-1,3,5 - triazin - 6 - ylamino) - 3 - sulpho - 2 - (4 - sulphophenylazo)-1-naphthol disodium salt. The dyes can be copolycondensed with bis(hydroxymethyl)urea, NN'-bis-(methoxymethyl)urea, tetrakis(hydroxymethyl)acetyl-diurea, bis(hydroxymethyl)ethyleneurea and tri(hydroxymethyl)melamine resins, and the resins can combine with OH-groups of fibres when these dyes are absorbed by cellulosic fibres together with a catalyst [$(NH_4)_2HPO_4$] and any precondensate of an amino-formaldehyde resin, the dyeings being baked at 140–150°C for 10–20 min.
C.O.C.

Imidazole Dyes. III— Reaction of *sym*-Tetra-aminobenzene with Carboxylic Acids
J. Arient, J. Marham, and H. Täublová

Collection Czechoslov. Chem. Communs., 25 (1960) 1602–1611 (*in German*)
Chem. Abs., 54 (10 Sept 1960) 17381

A study of the condensation under various conditions of 1,2,4,5-$C_6H_2(NH_2Cl)_4$ with formic acid, acetic acid, acetic anhydride, $C_6H_5CH_2COOH$, C_6H_5CH:CHCOOH, BzOH, BzCl, p-$O_2NC_6H_4COOH$, and 1,8-$C_{10}H_6(COOH)_2$.
C.O.C.

Colour Formers containing a *m*-Alkylphenoxyacyl Group
General Aniline
BP 852,922 (U.S.A. 4 Sept 1957)

Compounds of formula—
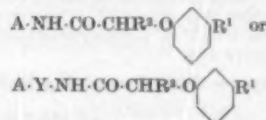
(R^1 = Alk of 10–20 C; R^2 = H or Alk; A = a reactive methylene or phenolic hydroxyl group; Y = –CO·NH-alkylene-, –CO·NH·arylene-, –NH–arylene or arylene), e.g. 4,6-dichloro-2-[α(3′-n-pentadecylphenoxy)-n-butyramido]phenol, are colour formers of low m.p. and very high solubility in water-immiscible organic solvents. C.O.C.

Azo Compounds Produced by Means of Organic Azides
Agfa
BP 854,955 (Germany 20 Nov 1956)

Compounds containing a methylene group, e.g. acyl-acetic ester or amides, pyrazolones, phenols, naphthols, etc., react with organic azides (especially sulphonyl azides), to give azo compounds, thus—

$$\begin{array}{c} X^1 \\ Y^1 \end{array}\!\!> CH_2 + N_3R \rightarrow \left[\begin{array}{c} X^1 \\ Y^1 \end{array}\!\!> CH_2 \cdot N_3R\right]$$

$$\left[\begin{array}{c} X^1 \\ Y^1 \end{array}\!\!> CH_2 \cdot N_2R\right] + \begin{array}{c} X^2 \\ Y^2 \end{array}\!\!> CH_2 \rightarrow \begin{array}{c} X^1 \\ Y^1 \end{array}\!\!> CH \cdot N:N \cdot CH <\!\!\begin{array}{c} X^2 \\ Y^2 \end{array}$$

(R = Ar, Alk, etc., but preferably Alk·SO₂, Ar·SO₂ etc.; X¹,X²,Y¹,Y² = electropositive groupings, e.g. CH:CH, CO, CN or together, form isocyclic or heterocyclic rings). Thus 2-chlorobenzoic acid-5-sulphonyl chloride condensed in methanol with sodium azide in presence of aq. NaOH gives the sulphonyl azide, which when stirred in methanol with 3-methyl-1-phenyl-5-pyrazolone in presence of sodium acetate gives the azo compound—

$$CH_3 \cdot C - CH \cdot N:N \cdot CH \cdot C \cdot CH_3$$

(with N—CO   OC—N pyrazolone rings, N₄)
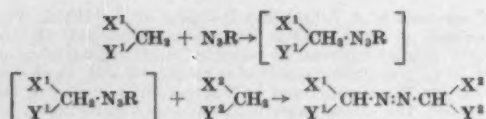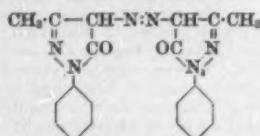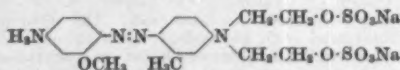
E.S.

Azo Acid Dyes having a Triazine Ring
BASF   BP 854,158 (Germany 31 Aug 1957)

The title dyes are condensates of cyanuric chloride with aminoazo compounds, and contain at least one OH group esterified with sulphuric acid or with an arylcarboxylic acid containing SO₃H as a substituent, but no other SO₃H group. At least one Cl atom in the cyanuric ring is left unchanged, but one Cl atom may be condensed with e.g. the sulphuric ester of monoethanolamine. Thus 1 mol. of the monoazo compound—

$$H_2N\!\!-\!\!\bigcirc\!\!-\!\!N:N\!\!-\!\!\bigcirc\!\!-\!\!N\begin{array}{c}CH_2 \cdot CH_2 \cdot O \cdot SO_3Na \\ CH_2 \cdot CH_2 \cdot O \cdot SO_3Na\end{array}$$
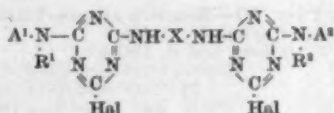(OCH₃   H₃C)

condensed with 1 mol. of cyanuric chloride gives a bright orange for wool and nylon.   E.S.

Reactive Azo Dyes for Cellulose
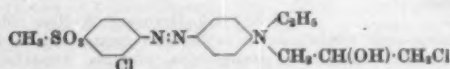ICI   BP 854,432 (5 Mar 1958)

Dyes of formula—

$$A^1 \cdot N \!-\! C\begin{array}{c} N \\ \\ N \end{array}C \cdot NH \cdot X \cdot NH \cdot C\begin{array}{c} N \\ \\ N \end{array}C \cdot N \cdot A^2$$
(R¹   N   Hal ... N   R²   Hal)

(X = alkylene of > 1 C, or phenylene or diphenylene which may carry substituents; R¹,R² = H or Alk; A¹,A² = residue of soluble azo compounds free from complexly bound metal and from groupings imparting capacity to form metal complexes, and are preferably monoazo compounds of the phenylazonaphthalene or phenylazopyrazolone series) react with cellulose in presence of acid-binding agents and have good building-up powers and stability to storage. Thus the monoazo compound orthanilic acid → H acid (alkali-coupled) is condensed with 1 mol. of cyanuric chloride as described in BP 785,222 (J.S.D.C., 74 (1958) 58). Two mol. of the product are then condensed with 1 mol. of p-phenylenediamine to give a bright red reactive dye.   E.S.

Monoazo Disperse Dyes Containing Halogenohydrin Groups
ICI   BP 855,715 (4 Sept 1958)

Benzene-series primary arylamines containing substituents such as CN, COAlk, SO₂·NH₂, SO₂Alk, etc. are diazotised and coupled with N-γ-chloro(or bromo)-β-hydroxypropyl derivatives of benzene- or naphthalene-series arylamines to give yellow, orange, and red disperse dyes. Thus diazotised 4-amino-3-chlorophenylmethyl sulphone is coupled with N-ethyl-N-(γ-chloro-β-hydroxypropyl)aniline to give—

$$CH_3 \cdot SO_2\!\!-\!\!\bigcirc\!\!-\!\!N:N\!\!-\!\!\bigcirc\!\!-\!\!N\begin{array}{c}C_2H_5 \\ CH_2 \cdot CH(OH) \cdot CH_2Cl\end{array}$$
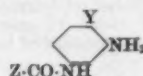(Cl)

which dyes cellulose acetate and nylon scarlet.   E.S.

Monoazo Compounds Containing a Dichlorotriazine Residue— Reactive Dyes for Cellulose
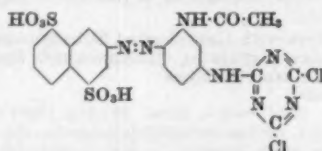Ciba   BP 855,792 (Switzerland 6 Sept 1956)

Aniline or naphthylamine sulphonic acids containing at least 1 SO₃H for each 6-membered ring present are diazotised and coupled with m-aminoacylanilides—

$$\begin{array}{c} Y \\ \bigcirc \\ Z \cdot CO \cdot NH \end{array}\!\!NH_2$$

(Y = H, Alk, or OAlk of < 3 C; Z = CH₃, C₂H₅, CH₂OH, OCH₃, OC₂H₅ or NH₂) and the resulting aminomonoazo compounds are condensed with 1 mol of cyanuric chloride to give yellow and orange reactive dyes for cellulose. Thus, 2-naphthylamine-4,8-disulphonic acid is diazotised and coupled with m-aminoacetanilide, and the product is condensed at 0–5°C with cyanuric chloride, giving—

$$HO_3S\!\!-\!\!\bigcirc\!\!\bigcirc\!\!-\!\!N:N\!\!-\!\!\bigcirc\!\!-\!\!NH\cdot CO \cdot CH_3 \;\; NH \cdot C\begin{array}{c}N \\ \\ N\end{array}C\cdot Cl$$
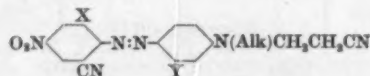(SO₃H ... N=C=N, C, Cl)

which dyes cotton yellow from an alkaline bath.   E.S.

Disperse Dyes for Dyeing and Printing Polyester Fibres
S   BP 855,488 (Switzerland 30 Apr 1958)

Dyes of formula—

$$O_2N\!\!-\!\!\bigcirc\!\!-\!\!N:N\!\!-\!\!\bigcirc\!\!-\!\!N(Alk)CH_2CH_2CN$$
(X ... CN ... Y)

(X = H, Cl or Br; Y = H or CH₃; Alk of 1–4 C) readily give dischargeable bluish red to violet dyeings on polyester fibres from aqueous dispersion. The dyeings have very high fastness to light; thus, a dyeing of 1/25 of standard depth is many times better than that of closely related dyes of only slightly different constitution. The dye 4-nitro-2-cyano-4′-(N-cyanoethyl-N-ethyl)-amino-1,1′-azo benzene dyes Terylene a bluish red fast to light, washing, water, seawater, perspiration, gas fumes, sublimation, heat setting and pleating, and dischargeable to white.
C.O.C.

Metal(Chromium)-complex Monoazo Dyes for Wool
Gy   BP 853,998 (Switzerland 29 Mar 1957)

N-benzoyl and -benzenesulphonyl derivatives of 1-amino-7-naphthol, the acyl groups containing alkylsulphonyl or sulphonamide substituents, are coupled with suitable diazotised o-aminophenols to give monoazo compounds whose 1:2 Cr complexes dye wool olive and grey of high light fastness from neutral baths. Thus 2-amino-4-nitrophenol diazotised and coupled with N-p-methylsulphonylbenzoyl-1-amino-7-naphthol gives—

$$O_2N\!\!-\!\!\bigcirc\begin{array}{c}OH \;\; HO \\ N:N \\ HN \\ CO \\ \bigcirc \\ SO_2 \cdot CH_3\end{array}\!\!\bigcirc\!\!\bigcirc$$
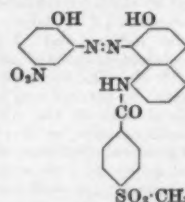
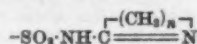whose 1:2 Cr complex is green olive.   E.S.

Metal-complex Monoazo Dyes for Wool, etc., having Cyclic Sulphonamidine Residues
BASF   BP 853,786 (Germany 22 Dec 1956)

Complexes of 1 atom of metal (e.g. Co or Cr) and 2 mol. of metallisable monoazo compounds free from SO₃H groups but containing a group—

$$-SO_2 \cdot NH \cdot C\begin{array}{c}\overline{(CH_2)_n}\\=\!\!=\!\!N\end{array}$$

($n = 3$–7), or 1 mol. of such a compound and 1 mol. of other suitable monoazo or azomethin compounds are faster to alkaline wet treatments on wool and nylon than similar dyes having simple unsubstituted sulphonamide groups. Thus 2-naphthol-6-sulphonamide is refluxed in ethanol containing pyridine with caprolactam-O-methyl ether to give—
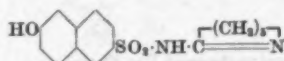

with elimination of CH_3OH. Coupling with diazotised 2-amino-4-chlorophenol gives the *oo'*-dihydroxymonoazo compound, converted by stirring at 80°C with aq. $CoCl_2$ into the complex, which dyes wool and nylon reddish violet.　　E.S.

Yellow and Orange Monoazo Direct Dyes Having Triazole Rings
FBy　　　　　　　*BP* 853,013 (Germany 11 July 1957)
The title dyes have formula—
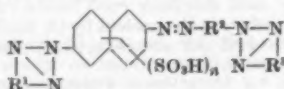
(R^1, R^2 = residues of naphthylamine coupling components; R^3 = residue of benzene- or naphthalene-series Ar in which the triazole and azo groups are in *p*-position to each other; n = 1 or 2). Thus the *o*-aminoazo compound 6-nitro-2-naphthalene-4,8-disulphonic acid → 2-naphthyl-amine-6-sulphonic acid is heated with ammoniacal $CuSO_4$ to give the triazole. The nitro group is then reduced to NH_2 with iron, and the product is diazotised and coupled with *m*-toluidine. Diazotisation and coupling with 2-naphthylamine-6-sulphonic acid follow, and treatment with ammoniacal $CuSO_4$ then gives a second triazole ring, the product being—
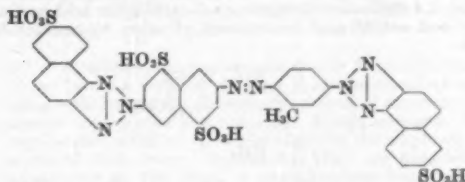
which dyes cotton yellow.　　　　　　E.S.

Metal(Chromium and Cobalt)-complex Monoazo Dyes for Wool from 4-Hydroxydiphenyl
BASF　　　　　　*BP* 852,689 (Germany 24 Jan 1957)
Monoazo compounds obtained by diazotising an *o*-methoxyarylamine of the benzene or naphthalene series and coupling with 4-hydroxydiphenyl (I) are converted into 1 : 2 chromium or cobalt complexes (either alone or in admixture with other suitable coloured or colourless complex-forming compounds), which dye wool from weakly acid baths, or may be used for colouring lacquers, etc. Compared with similar dyes from 4-alkylphenols, they have better substantivity and wet fastness, and compared with similar dyes from *β*-naphthol, better wet fastness and level-dyeing properties. Thus the monoazo compound 2-aminoanisole-4-sulphonamide → I is heated with cobalt acetate in acetamide at 130°C to give a bordeaux.　　E.S.

Metal(Chromium and Cobalt)-complex Amino-monoazo Dyes for Wool etc.
ICI　　　　　　　　*BP* 853,172 (30 July 1958)
Metallisable nitromonoazo dyes are complexed with Co or Cr and then treated with a soluble salt of H_2S to give the title dyes in higher yields and purer state than by the combined metallisation and reduction process of *BP* 295,594 (J.S.D.C., **46** (1930) 87). The products may react at the amino group with, e.g., acetyl chloride, or the metal may be removed by means of oxalic acid to give dyes not readily prepared in good yields by more direct syntheses. Thus the monoazo compound 2-amino-6-nitrophenol-4-sulphonic acid → *β*-naphthol is stirred at 90–100°C with aq. chromium acetate for 30 min. After cooling to 80°C, Na_2S is added to give the required amino-azo dye chromium complex.　　　　　　E.S.

Lakes of Monoazo Dyes
S　　　　　　　*BP* 853,778 (Switzerland 16 May 1957)
Monoazo compounds obtained by coupling diazotised aniline- or naphthylamine-monosulphonic acids with *N*-acylacetoarylamines free of water-solubilising groups are laked with water-soluble salts of divalent or multi-valent metals to give yellow pigments of good fastness to heat and solvents. Thus diazotised 3-amino-6-chloro-toluene-4-sulphonic acid is coupled with *N*-acetoacetyl-*o*-anisidine to give—
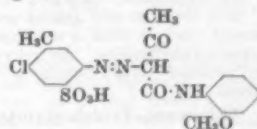
Stirring at 80°C with aq. $CaCl_2$ gives the lake which colours polyvinyl chloride in the mass greenish yellow.　　E.S.

### Metallisable Azo Dyes from Keto Derivatives of Resorcinol
FH　　　　　　　*BP* 854,404 (Germany 17 Dec 1955)
Ketones derived from resorcinol—
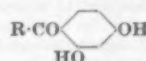
(R = Alk of 1–6 C or cycloalkyl) are coupled with diazotised *o*-aminophenols, anthranilic acids, etc. to give mono- and dis-azo dyes which may be metallised in substance or on the fibre. Thus 2-amino-6-nitrophenyl-4-sulphonic acid diazotised and coupled with 2,4-di-hydroxyphenylmethylketone is a garnet afterchrome dye for wool, and its Cr complex dyes leather reddish violet.　　　　　　E.S.

Trisazo Blacks for Leather
YDC　　　　　　　*BP* 854,957 (28 Jan 1958)
Trisazo dyes—
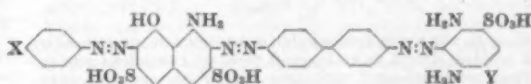
(X = H, CH_3 or SO_3H; Y = Hal, CH_3, OCH_3 or SO_3H) give well-penetrated blacks on chrome-tanned leather. Thus tetrazotised benzidine is coupled with 1 mol. of H acid under weakly acid conditions, and 1 mol. of diazotised aniline is then coupled on to the product. Finally the diazo–disazo compound so formed is coupled with 2,4-diaminotoluene-5-sulphonic acid.　　　　　　E.S.

Water-soluble Reactive Dyes
ICI　　　　　　　　*BP* 854,962 (19 May 1958)
Dyes containing at least one group—

$$-Z \cdot CH_2CH \cdot CH_2X \quad \text{or} \quad -Z \cdot CH_2 \cdot CH \cdot CH_2$$
$$\underset{OH}{} \qquad\qquad\qquad \underset{O}{}$$
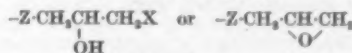
(Z = O, S or SO_2, X = Cl or Br) are reactive dyes for cellulosic fibres and have excellent washing fastness. They may be azo, anthraquinone or phthalocyanine dyes, especially those containing a 3-chloro-2-hydroxypropoxy group, and the preferred type is—
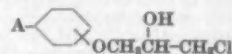
(A = *N*-naphthylazo, *N*-naphthylazopyrazolonyl, *N*-anthraquinonylamino or *N* - Cu phthalocyanine sulphamyl radical, containing 1–3 SO_3H groups). Thus, Cu phthalocyanine tetra - 3' - sulphonchloride obtained by treating Cu phthalocyanine (C.I. 74160) (23) with $ClSO_3H$ (240) at 138°C for 4 h is suspended in water (400) at < 5°C at pH 7·0. 4-(3'-Chloro-2'-hydroxypropoxy)-aniline (16·1) in water (50) and HCl (s.g. 1·16) (8·1) are added, followed by $NaHCO_3$ (34). After stirring for 5 h at 5°C and 12 h at 20°C, the product is filtered off. It contains < 2 SO_3H groups and 1·5–2·2-sulphon-4-(3'-chloro-2'-hydroxypropoxy)anilide) groups/mol. and dyes cellulosic fibres greenish blues of excellent washing fastness when applied in conjunction with an alkali.　　A.T.P.

Leuco Sulphuric Esters of Anthraquinone Vat Dyes

FH *BP* 853,264 (Germany 15 Feb 1956)

Finely dispersed anthraquinone vat dyes which are difficult to esterify (e.g. anthraquinone carbazoles, anthrimides, subst. or unsubst. 1-aroylamino or bis-aroylaminoanthraquinones) are treated with Zn dust, Fe or Cu powder and a hydrogen halide, or an anhydrous saturated unsubst. or halogenated aliphatic carboxylic acid. The resulting leuco compound is finally sulphated. Thus, 1,1',5,1'' - trianthrimide - 2,2',6,2'' - carbazole is reduced at 40°C with Zn dust and glacial acetic acid and the leuco compound treated with a mixture of ethylene chloride, 4-chlorodimethylaniline, dimethyl formamide and SO₃. The product dyes cotton a clear yellow of excellent fastness. A.T.P.

## Water-soluble Thiocyano-Triazinylamino Reactive Dyes

ICI *BP* 852.911 (12 Feb 1958)

The title cpd. are water-soluble coloured amino compounds where the NH₂ group is substituted by a s-triazine group containing at least one –SCN group on one C atom and optionally on the other C, alkyl, aryl, halogen and preferably another –SCN group. They are reactive dyes which on nylon and cellulosic fibres give dyeings of excellent fastness to washing. Thus, 2-chloro-4,6-dithiocyano-s-triazine is condensed with the di-Na salt of the azo dye 2-naphthylamine-4,8-disulphonic acid → m-toluidine to give a product containing no combined chlorine and two SCN groups on the triazine ring. It dyes cotton yellow, fast to light and washing. A.T.P.

Iso-Indolone Dyes

Gy *BP* 853,237 (Switzerland 17 Dec 1957)

2-Cyanobenzoic acid esters containing 3–4 Hal react with NH₃, an alkali-metal amide or a primary amine to give polyhalogeno-3-imino-isoindoline-1-ones—
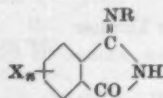

(R = H, aliphatic, cycloaliphatic, araliphatic, or aromatic; X = Hal; n = 3 or 4), in good yield and excellent purity. These are condensed with poly primary homo- or heterocyclic aromatic amines or hydrazine to give the title compounds. They are yellow, orange, and red pigments of good tinctorial strength and fastness to heat, light, and migration; cf. *BP* 833,548 (J.S.D.C., **76** (July 1960) 457). A.T.P.

Red Anthraquininoid Disperse Dyes

Eastman Kodak *BP* 854,098 (U.S.A. 10 Mar 1958)

Dyes of excellent fastness to light, gas fumes, sublimation and solvent rubbing have formula—
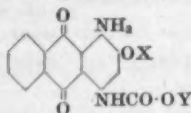

(X = CH₃, C₂H₅, C₃H₄OCH₃ or C₂H₄OC₂H₅; Y = Alk of 4–8 C or cyclohexyl). They are obtained by condensing 1-4-diamino-2-OX-anthraquinones with haloformic esters Z·COOY (Z = Cl or Br). Thus, 1,4-diamino-2-methoxyanthraquinone (10) is refluxed in ethylene glycol monomethyl ether (100) with n-amylchloroformate (10) until HCl ceases to evolve. After CH₃OH has been added and the mixture cooled to 0°C, the product (X = CH₃, Y = n-C₅H₁₁) is filtered off. It dyes polyester and cellulose acetate fibres bright red with excellent fastness. A.T.P.

Anthraquinone Vat Dyes

Gy *BP* 853,969 (Switzerland 11 July 1956)

The compounds obtained by condensing 3 equiv. of a vattable aminoanthraquinone with C₆H₅-(-C₆H₄·COX-p)₃ (X = OH or halogen) are greenish yellow, orange, red, violet, and blue "hot-dyeing" vat dyes of excellent fastness. Thus, 1,3,5-triphenylbenzene-4',4'',4'''-tricarboxylic acid chloride is condensed (in, e.g., trichlorobenzene, nitrobenzene) with 3 mol. of 1-aminoanthraquinone to give a greenish yellow dye, and with 3 mol. of 4-aminoanthraquinone-3',5'-dichloro-2,1-(N)-1',2'-benzacridone to give the blue dye—
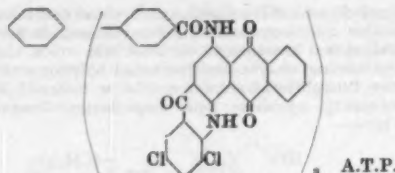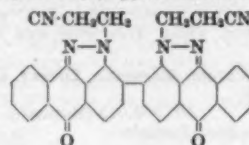

Red Dipyrazolanthronyl Vat Dyes

General Aniline *BP* 855,710 (U.S.A. 28 Dec 1955)

NN'-bis-(β-cyanoethyl)dipyrazolanthronyls—

which may be subst. in the nucleus by Cl, Br, NH₂, CH₃ or C₂H₅, are obtained by reaction of acrylonitrile with dipyrazolanthronyls in presence of an organic quaternary nitrogen base, e.g. tetraethanol ammonium hydroxide, in an inert organic solvent, e.g. t-C₄H₉OH, at 25–100°C. They are dark red vat dyes of excellent washing, light, and chlorine fastness and are readily converted to leuco sulphuric ester salts. A.T.P.

1,3,4-Oxdiazoles— Fluorescent Brightening Agents, Dyes and Intermediates

BASF *BP* 855,721 (Germany 20 Mar 1958)

Imido-ether salts react readily with monoacyl hydrazides at 70–180°C in presence of solvent and/or diluent, e.g. N-methylpyrrolidone, ethanol, nitrobenzene, to give 1,3,4-oxdiazoles in good yield and excellent purity. They are fluorescent brightening agents, intermediates and dyes for natural and regenerated cellulose and polyamides. Thus, 1,4-diaminoanthraquinone-2-carboxylic acid hydrazide and acetic acid bis-imidoethyl ether hydrochloride give
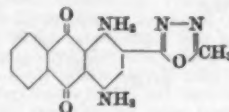
a blue disperse dye for nylon. Similarly, 1-aminoanthraquinone-2-carboxylic acid hydrazide and succinic acid bis-imidoethyl ether hydrochloride give
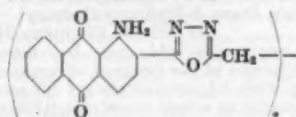
a strong-dyeing red vat dye. A.T.P.

Hydron Blue Dyes

General Aniline *USP* 2,921,830 (31 July 1956)

Ready to dye sulphur dyes in stable aqueous emulsion are obtained by refluxing carbazole indophenol (12–35), water (15–120), an aliphatic hydroxy compound of 1–10 C (20–105), NaOH (0–40), Na₂S (4–20), S (20–85) and an ionic or non-ionic surface-active agent (3–15), cooling to 100°C and diluting in a 2:1 ratio with 20–22% aq. Na₂S. The method is more economical than standard methods and the products are stable to oxidation and easily standardised; they do not salt out or separate on cooling and dye brighter and greener than Hydron Blue obtained by conventional methods. A.T.P.

Salt-like Dyes for Acrylic Fibre Blends

BASF *BP* 853,955 (Germany 18 Apr 1956)

Title cpd. are [K]⁺[A]⁻ where K is the cation of a cationic dye (I) component, e.g. polymethin dye, and A the anion of an anionic dye (II) component, e.g. phthalocyanine, di- and tri-arylmethane, anthraquinone, mono- and poly-azo dyes and their metal complexes. They are prepared by precipitating a solution of I with a solution of II, or vice versa, or by grinding I and II to a paste with water, drying and powdering, preferably in presence of a

dispersing agent. The dyes give solid or two-tone dyeings of excellent fastness on fibre mixtures containing an acrylic fibre and any fibre capable of being dyed with II. Thus, a disperse dye is made from equal amounts of—
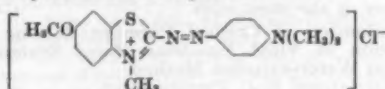
and
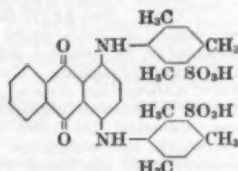
It dyes the above fibre mixtures blue with excellent fastness.   A.T.P.

Naphthylene Benzimidazole Vat Dyes
FH   *BP* 854,162 (Germany 4 Jan 1956)

Mixtures of isomers—
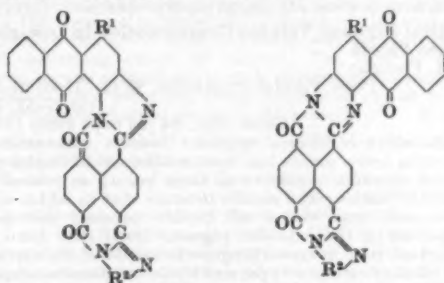
(R^1 = H, alkoxy, benzamido, chloro- or fluoro-benzamido, R^2 = benzene residue, the two N atoms attached to R^2 being *ortho* to one another) are vat dyes of excellent fastness to boiling soda and have high dyeing strength. They may be converted by known methods to the sulphuric acid esters of their leuco compounds. They are obtained by condensing at 180–220°C a naphthoylene benzimidazole *peri*carboxylic acid or anhydride with a 1,2-diamino-anthraquinone (I) containing group R in the 4 position, or with a 1-(or 2-)-nitro-2-(or 1-)aminoanthraquinone similarly substituted, followed by treatment with a hot reducing agent, when ring closure to the benzimidazole occurs. If condensation with I is effected in a low-b.p. solvent, an intermediate product can be isolated, convertible at elevated temp. to the dye. Thus naphthoylene benzimidazole *peri*dicarboxylic acid anhydride (340) and 1,2-diaminoanthraquinone (250) are heated at 310°C for 15 h in trichlorobenzene (3000) to give a copper–brown vat dye of excellent fastness to washing, Cl_2, boiling soda and light.   A.T.P.

Pyrrole Intermediate and Fluorescent Brightening Agents
Ciba   *BP* 853,129 (Switzerland 31 July 1956)

Pyrrole derivatives—
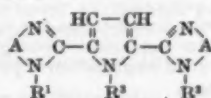
(A = subst. or unsubst. benzene, R^1 and R^2 = H or same or different alkyl, alkenyl or hydroxyalkyl, R^3 = H, acyl subst. or unsubst. Alk, alkenyl, cycloalkyl, aryl, aralkyl or heterocyclic residue) and their quaternary NH_4 salts are dye intermediates and fluorescent brightening agents, and may be used to render organic materials opaque to ultraviolet radiation. Thus, the di-imidazole—

(from the acid K salt of saccharic acid and o-phenylene-diamine) is condensed with urea to give 92·6% of 2,5-di-[benzimidazyl-(2)]-pyrrole, a fluorescent brightening agent for polyacrylonitrile fibres.   A.T.P.
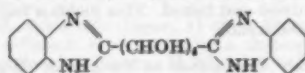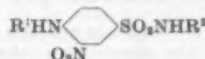
Diphenylamine Disperse Dyes
Celanese Corpn. of America

USP 2,921,945 (17 May 1954)

Yellow disperse dyes of excellent washing fastness are—

(R^1 and R^2 = subst. or unsubst. aryl, one of which carries COOH) and are obtained by known methods. Fibres dyed with them can be further treated with cationic resin-forming materials or metallic compounds to further increase washing fastness. Thus, p-aminobenzoic acid is condensed with 4-chloro-3-nitrobenzenesulphonyl chloride and the condensate treated with aniline to give—
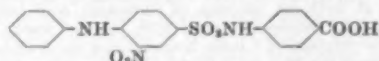
a fast-to-washing yellow, preferably applied to cellulose acetate and nylon at pH 5·5–6·0.   A.T.P.

Water-soluble Phthalocyanine Dyes
BASF   *BP* 853,364 (Germany 20 May 1958)

The title compounds—
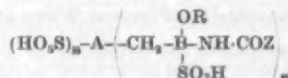
(A = phthalocyanine residue; B = aromatic residue containing $\ngtr$ 2 benzene nuclei; R = H, CH_3 or C_2H_5; m = 1–8; n = 0–4; Z = subst. or unsubst. vinyl) are characterised by outstanding light fastness. They are obtained by reaction of a compound of above structure where NH·COZ is replaced by NH_2 with acryloylating agents, e.g. acrylic acid chloride, maleic anhydride. Thus, tetrakischloromethyl Cu phthalocyanine is condensed with m-toluidine in sulphuric acid monohydrate until the product is soluble in dilute NaOH. After further reaction in presence of H_2SO_4, the mass is filtered off and the cake treated with acrylic acid chloride to give a water-soluble greenish blue dye for cotton, of excellent fastness, especially to light.   A.T.P.

Solvent-resistant α-Copper Phthalocyanine (C.I. 74160)
Ciba   *BP* 855,098 (Switzerland 5 Oct 1956)

Cu phthalocyanine (3 parts by wt.) either in α- or β-form is heated in an inert organic solvent of b.p. $\ngtr$ 100°C with isophthalic or terephthalic acid dichloride ($\ngtr$ 1) in presence of anhydrous $AlCl_3$. This yields an α-form pigment of much greater resistance to solvents than that obtained by heating Cu phthalocyanine to 180°C in trichlorobenzene with anhydrous $AlCl_3$.

C.O.C.

Phthalocyanine Sulphur Dyes
CFM   *BP* 854,579 (Germany 19 Apr 1958)

Phthalocyanines or their metal derivatives react with a mixture of 50–90% of H_2SO_4 monohydrate and 50–10% of $ClSO_3H$, and hydroxylamine salts or primary ω-nitro-paraffins of chain length $\ngtr$ 4 C atoms in presence of a compound of an element of Periodic Groups Va or VIa at 70–150°C. The resulting polyaminophthalocyanines then react *in situ* with > 5 mol. S_2Cl_2. The neutral grey dyes have higher light fastness than the olive grey dyes of *BP* 848,880 (*J.S.D.C.*, **77** (Jan 1961) 37), which employs $ClSO_3H$ alone.   A.T.P.

β-Carotene (C.I. 75130) and closely related Carotenes
Koninklijke Nederlandsche Gisten Spiritusfabriek

BP 854,419 (U.S.A. 18 Feb 1957)

β-Carotene is produced by growing plus and minus types of *Choanephora cucurbitarum* (or other species of *Mucorales*) simultaneously in a liquid medium containing glucose, acid-hydrolysed casein, mineral salts, and thiamine. The yield is much increased if β-ionine and/or an assimilable lipid and/or surfactant is present and the cultures are incubated under submerged aerobic conditions at 20–30°C and initial pH 5–7.   C.O.C.

Alkaline-earth-metal Silicates
Columbia-Southern Chemical Corpn.

BP 855,014 (U.S.A. 13 Mar 1956)

Pigmentary, amorphous, hydrated, calcium silicate is obtained by treating an aqueous solution of an alkaline-earth-metal salt, e.g. $CaCl_2$, and an alkali-metal silicate, e.g. Na silicate. To obtain a pigment of surface area 5–20 m²/g, the strength of $CaCl_2$ solution must throughout the process be maintained at 0·4–5·0 mole % stoichiometric excess.

BP 855,015 (U.S.A. 13 Mar 1956)

Precipitation of the pigment is accelerated by adding to the slurry formed by the above process, enough of a water-soluble alkaline-earth-metal salt to make ≮ 0·15 mole of the salt per mole of alkaline-earth-metal silicate.
C.O.C.

Silica (C.I. Pigment White 27)
Columbia-Southern Chemical Corpn.

BP 854,014 (U.S.A. 30 Sept 1957)

A silica pigment has its bound water content reduced by treating it with an amount of inorganic acid halide in excess of that required to react with the free water. Thus a pigment containing 1 mole bound water per 6 moles SiO_2 was refluxed for 12 h with 60 ml of $SiCl_4$. After the $SiCl_4$ was distilled off *in vacuo*, an acid pigment was left which was readily neutralised with ammonia or an amine, e.g. when 80 ml of diallylamine were added to the dry pigment and heated at 50–80°C for 4 h, followed by washing with methanol and extraction with ether, a hydrophobic pigment was obtained.
C.O.C.

Titanium Dioxide (C.I. Pigment White 6)
I.T
BP 853,959 (21 Feb 1957)

Ti(OH)₄ precipitated by hydrolysis of a Ti salt in aqueous solution is heated at ≯ 800°C to remove water. The dried precipitate is then calcined while being maintained in a fluidised condition by a stream of hot non-reducing gas.
C.O.C.

Rutile Titanium Dioxide (C.I. Pigment White 6)
Glidden Co.
BP 854,933 (U.S.A. 13 Jan 1958)

A stable colloidal rutile-inducing and yield-inducing seed, especially suitable for use in hydrolysing aqueous titanium sulphate, is obtained by mixing purified ortho-titanic acid with (*a*) a source of fluoride ions and (*b*) HCl, HBr, HI or HNO_3 and then curing the mixture. C.O.C.

Sighting Colours derived from Reactive Anionic Dyes (VI p. 81)

Accelerated Fading of Certified Dyes in Presence of Non-ionic Surfactants (XIV p. 87)

V— PAINTS; ENAMELS; INKS

Action of Ultraviolet Radiation and its Absorption in Resins and Pigmented Materials
M. Gieson
Chim. peintures, 23 (1960) 69–81
Chem. Abs., 54 (10 Sept 1960) 17905

Study of the ultraviolet absorption spectra of 2,4-dihydroxybenzophenone (I), 2-hydroxy-4-methoxybenzophenone (II), 2,2′,4,4′-tetrahydroxybenzophenone (III), 2,2′ - dihydroxy - 4,4′ - dimethoxybenzophenone (IV), 2-hydroxy-4′-methylbenzophenone (V), 2-hydroxy-5-chlorobenzophenone (VI), phenylsalicylate (VII), t-butyl salicylates (VIII), derivatives of cinnamyl aldehyde (IX) and of benzotriazole (X), to find out significant differences between them in protecting resins and pigmented materials from ultraviolet radiation. I, VI, VIII, X, and a mixture of IV and other tetra-substituted benzophenones were each incorporated into polystyrene and polyvinyl chloride and exposed in an Atlas Fade-O-Meter for 60 h. A control containing no ultraviolet absorber accompanied each sample. Results are given as colour photographs, tables and graphs. The absorbers were incorporated into the resins by dissolving the mixture in methylethyl ketone and evaporating off the solvent. Measurements were made on 9-μ thick films at 460 mμ. Absorption in the blue region indicates yellowing. In polystyrene, least discoloration occurred in presence of II and most in presence of IX. In polyvinyl chloride, least discoloration was with IX, and most with the mixture containing IV. II (1%) in a mixture of Toluidine Red (C.I. Pigment Red 3) and nitrocellulose lacquer prevented fading of the dye; 0·5% was insufficient. When I, VI, VIII, and IX and the mixture

containing IV were added to low-viscosity nitrocellulose, acrylic or polyester resin, no noticeable colour change occurred. Marked differences were shown in the values of the same absorber for different resins and for different absorbers in the same resin.
C.O.C.

Determination of Critical Pigment Volume Concentration of Vinyl Emulsion Paint Systems by Pigment Water-sorption Method
F. P. Liberti and R. C. Pierrehumbert
Amer. Paint J., 42 (44) (1958) 28–51
Chem. Abs., 54 (25 Sept 1960) 18977

Water-sorption values of both prime and extender pigments were established by titration with a solution of Tamol 731 and K tripolyphosphate. They are used for simple calculation of a theoretical critical pigment volume concentration (CPVC). A series of pigments and pigment combinations was evaluated for CPVC by scrub test method, tensile strength, and elongation. The test data show that theoretical CPVC calculated from the water-sorption value approximates within ± 3% that obtained by the above methods. The particle size of the emulsion does not necessarily affect the CPVC. While water-sorption values can be used to determine the CPVC of a vinyl acetate copolymer paint, this determination is useful only in establishing proper balance of pigment to resin solids so as to obtain optimum paint properties. C.O.C.

Critical Pigment Volume Concentration in Low-gloss House Paints
T. H. Ferrigno
Paint Varnish Production, 50 (3) (1960) 31–35;
(5) 47–51, 102
Chem. Abs., 54 (25 Sept 1960) 18979

The effect of critical pigment volume concentration (CPVC) in house paints has been studied to determine the rôle of extender pigments in these paints as related to excess of binder. The results indicate that in addition to CPVC and any excess of binder present, pertinent properties of the extender pigment itself may have an important part in controlling performance of the system. The effect of extender types and levels on blister resistance, brushing properties, staining, and hold out are cited.
C.O.C.

Molybdates: New Pigments for Primers
H. O. Schoen *Chem. Eng. News*, 38 (46) (14 Nov 1960) 58

A study comparing use as inhibiting primers of $CaMoO_4$, $ZnMoO_4$, and $5ZnO·7MoO_3$ (zinc polymolybdate) with that of Red Lead (C.I. Pigment Red 105), Zn chromate (C.I. Pigment Yellow 36) and iron oxide (C.I. 77491, 77492 and 77499). They have the advantages of being white and non-toxic. For use as a primer alone, $CaMoO_4$ showed better all-round performance than either of the Zn compounds. However, when a topcoat is given, the zinc compounds are superior to the Ca, $ZnMoO_4$ being the best. Generally, better results were obtained when the molybdates were extended with $ZnCO_3$ (C.I. 77950), talc (C.I. Pigment White 26) not giving such good results. The finer the molybdate particles the better the protection against corrosion. Linseed oil was a better vehicle than alkyd resin for the molybdates. Increasing the Zn:Mo ratio from 1:1 to 1:1·4 lowered the corrosion resistance.
C.O.C.

PATENTS

Polyester Resin Ink
Goodyear Tire & Rubber Co.
BP 855,066 (U.S.A. 30 Dec 1957)

Printing inks for high-mol.-wt. linear polymers contain as vehicle an ethylene terephthalate–ethylene isophthalate copolymer, the first component forming 75–30% of the copolymer. They yield tough, adherent prints. C.O.C.

Iridescent Coatings
Francis Earle Laboratories *USP* 2,922,724 (1 July 1957)

A layer of lamellae of high refractive index is applied from a liquid and then an interference film of plastic or resin is applied from a liquid. Thus a polyester pearl button is dipped into a 6·5% dispersion of Pearl Essence (C.I. Natural White 1) (crystals of average length 20 μ and thickness 50 mμ), dried and then dipped into a varnish of alkyd resin dry solids (3·2%) in xylol (96·8). The alkyd resin film is dried and baked. This yields a button having permanent iridescence.
C.O.C.

Phenylmercury Compounds as Fungicides (X p. 84)

VI— FIBRES; YARNS; FABRICS

Fibre Formation from Solutions of Collagen
II— The Rôle of Tyrosyl Residues
H. B. Bensusan and A. Scanu

J. Amer. Chem. Soc., **82** (20 Sept 1960) 4990–4995

Rate of fibre formation from soln. of iodinated collagen, prepared by treatment of buffered soln. of collagen with a slight excess of iodine at pH 8·2, was very much greater than that of untreated collagen. The product appeared to be normal collagen fibres. Activation energy for fibre formation fell by 50–57 kcal after iodination. It was concluded that ionisation of phenolic OH group of 8–10 tyrosyl residues occurred during activation step for fibre formation from soln. of untreated collagen.   F.J.

III— Some Effects of Environment on the Rate of Fibre Formation
H. B. Bensusan   *Ibid.*, 4995–4998

The effect of alcohols on the rate of fibre formation, measured by increases in optical density of collagen soln. buffered at pH > 7 has been studied. At low concn. of alcohol, the relative rate was decreased, particularly with n-propyl alcohol, the extent of the decrease being correlated with the activity coefficient of the alcohol. At higher concn. the rate became greater than the rate of fibre formation in the absence of alcohol and could be correlated with the decrease in dielectric constant of the medium. Activation energy of fibre formation was also decreased with increasing concn. of alcohol. The rate of fibre formation was reduced as the ionic strength of the medium decreased, this reduction being attributed to the lower activity of the charged groups in the protein.   F.J.

Studies on Rabbit Fibres. XXXV— Statistical Studies of Felting Factors
S. Ikeda   *J. Soc. Text. Cellulose Industr. Japan*, **16** (Sept 1960) 706–710

The following factors were found to be significant at the 5% level— (a) for carrotting, $[NaNO_2]$, $[HNO_3]$, immersion temperature, and drying temperature; (b) for felting, pH, sample temperature, pressure of the roller used in the felting apparatus, and the rate at which the direction of rotation of the roller is reversed.   M.T.

Studies on Acrylic Fibres
M. Takahashi and M. Watanabe

XVI— Interaction of Polyacrylonitrile with Solvents
J. Soc. Text. Cellulose Industr. Japan, **16** (Sept 1960) 711–715

Polyacrylonitrile monofilaments obtained by wet-spinning and cross-linked by radiation were swollen in various organic solvents. Values of μ, the polymer–solvent interaction parameter, were calculated using the Flory–Rehner equation for the swelling of cross-linked networks. For good solvents, a linear relation was found between this parameter and the solution temperature. Three tables (in English) list values of specific volume, equilibrium volume swelling ratio, interaction parameter, solution temperature, and cohesive energy density for 36 different solvents and for two solvent mixtures.

XVII— Solubility of Copolymers of Acrylonitrile and Acrylic Esters
Ibid., 715–718

The effect of copolymerisation on solution temperature was studied, using methyl, ethyl, and butyl acrylates as comonomers. Increasing the comonomer content decreased the solution temperature, a large decrease generally being found at low comonomer contents. The order of effect is Bu > Et > Me at low contents, but when the amount of comonomer exceeds ca. 10 mol. %, the degree of lowering of solution temperature is similar for all three comonomers.   M.T.

Action of Iodine on Polyamides
A. Cannepin and J. Rayon

Bull. Inst. Text. France, (89) (July–Aug 1960) 33–38

Adsorption of iodine by polyamide fibres can lead to structural changes which persist after removal of the adsorbed iodine. The treated fibres show modified dyeing behaviour.   J.C.F.

Self-diffusion of Surface-active Agents in Nylon
M. Hayashi

Bull. Chem. Soc. Japan, **33** (Sept 1960) 1184–1188

The self-diffusion rates of sodium dodecyl sulphate, sodium tetradecyl sulphate, H_2SO_4 and HCl in nylon containing various amounts of each solute, and their temp. dependence are measured by the surface radioactivity decrease method using ^{35}S and ^{36}Cl. The presence of water in nylon is necessary for diffusion to take place appreciably. In the sorption of surface-active agents and also of inorg. acids from their aq. soln. by nylon, not only the surface phenomenon but also the diffusion into the solid body is responsible for its progress towards equilibrium. It is opined that the interaction of ionic detergents and nylon takes place not only by ionic but also by van der Waals forces, since the amount of detergents taken up is also much larger than that of simple inorg. ions, which are considered to be bound to nylon mainly by ionic inter-action, and also much larger than the value corresponding to the amine content of nylon.   H.H.H.

Sighting Colours derived from Reactive Anionic Dyes
British Rayon Research Association

BP 848,459 (13 Mar 1957)

An azoic or anthraquinone reactive dye of low mol. wt. and containing solubilising sulphonate groups and either a mono- or di-chlorotriazinyl group is treated with a carbo-hydrate of high mol. wt., e.g. starch, in presence of alkali. The product is used in aqueous solution as a sighting colour for either natural or man-made fibres. The sighting colour is readily removed by simple scouring at a low temperature even when it has been pressure steamed.   C.O.C.

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Influence of Initial Bleaching Treatments on the Behaviour of Cotton Fabric subjected to Subsequent Bleaching Treatments
A. Parisot

Bull. Inst. Text. France, (89) (July–Aug 1960) 7–31

Cotton fabric was subjected to eight different initial bleach-ing treatments, and then sampled after repeated subsequent bleaching treatments. The latter included severe chemical treatments which reduced the DP of the cellulose but involved little mechanical action, normal industrial and domestic bleaching treatments, and a purely mechanical treatment with no bleaching. The relations found between mean DP and solubility index, and between mean DP and mechanical properties, were very similar to those found in an analogous study of linen fabrics (*Ibid.*, (82), 61; (83), 7). In contrast to the results obtained with linen fabric, there was some evidence that cotton fabric bleached with H_2O_2 showed better wear resistance than fabric bleached with sodium chlorite.   J.C.F.

Bleaching Cellulosic Fibres using Stable Solutions of Hydrogen Peroxide during Kier Boiling
N. E. Fedorova and P. V. Moryganov

Tekhnol. tekstil. prom., No. 4 (17) (1960) 129–137

A method for simultaneous kier boiling and bleaching at > 100°C has been developed. Conventional kiers can be used and there is no need for protective coating inside the kier. The suggested recipe (g/litre) is—

Sodium silicate sp. gr. 1·42	30
Caustic soda 100%	2
Wetting agent OP 10	0·2
Magnesium chloride	3
Hydrogen peroxide 100%	2

The process should be carried out at 110°C. Bleaching action is said to occur during heating to 40–80°C. At higher temp. the removal of nitrogenous impurities improves the absorbency of the cloth, but there is very little further bleaching. Under these conditions the hydrogen peroxide solution is stable. At the end of the process these are 0·07 g/l. of H_2O_2 and 4·6 g/l. of available alkali in the liquid.   L.S.L.

Assessment of "Softness" in a Synthetic Detergent by Biological Means
F. W. Roberts

Chem. and Ind., **42** (15 Oct 1960) 1282–1284

"Softness" is the ability of a detergent to be decomposed by bacteria associated with aerobic decay. The presence of "Hard", i.e. resistant, detergent has caused problems in sewage purification. "Hardness" in alkylaryl sulphonates is associated with the presence of tertiary alkyl groups in the molecule and may be assessed by infrared spectroscopy

after the use of a separation technique. In a biological method of assessment, the detergent is diluted to ca. 20 p.p.m. with Synthetic B.O.D. Water, seeded with 10% fresh soil suspension or sewage effluent and aerated for 3 days at 37°C. The detergent content is then re-determined, the percentage loss being regarded as "Soft". The results with various detergents were similar to those obtained by the infrared method. W.K.R.

Composition and Behaviour of Laundry Dirt
O. Oldenroth

II *Fette Seifen Anstrichmittel*, **61** (1959) 1220–1224
The principal component of the water-insoluble portion of laundry soil is skin fat. The accumulation of fatty material in various portions of cushions and inter- and under-garments was determined during various periods of use. Male clothing contained more fatty material than that of females. Yellowing of bedding and clothing was mainly caused by accumulation of fatty material from contact with the skin. Yellowing of clothing through repeated contact with skin fat was, in order of increasing amounts, polyester, polyamide, and cotton fabrics. The Fe content of water contributes to the yellowing of fabrics. Skin fat was more readily washed out by a mixture of fatty acid sulphate, Na_2CO_3, soap and phosphate from polyester and polyamide fabrics than from cotton fabrics. The synthetic polymers are not lipophilic.

III *Ibid.*, **62** (1960) 13–18
Chem. Abs., **54** (10 Sept 1960) 17923
Mercerised cotton absorbed less skin fat from solution than did ordinarily finished cotton and retained correspondingly less fat after repeated washing. Artificial soil was washed out more completely from polyester and polyamide fabrics by a fatty alcohol sulphate–Na_2CO_3 mixture than from cotton. C.O.C.
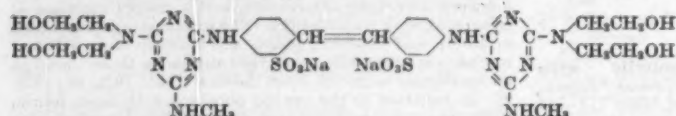
PATENT

Cotton Bleaching
FBy

BP 847,725 (Germany 7 June 1957)
The cotton is treated first with a fluorescent brightening agent and then given a "bundle bleach". Thus knitted cotton fabric is treated in a 20 : 1 bath containing 0·05 g/l. of the fluorescent brightening agent—

$$HOCH_2CH_2 \diagdown N-C \quad C\cdot NH-\langle CH==CH\rangle-NH\cdot C \quad C-N \diagup CH_2CH_2OH$$
$$HOCH_2CH_2 \diagup \qquad SO_2Na \quad NaO_2S \qquad \diagdown CH_2CH_2OH$$
$$NHCH_3 \qquad\qquad NHCH_3$$

It is then treated with an aqueous solution containing 3 g/l. Cl and 1·5 g/l. NaOH. Finally it is placed in a "bundle bleach" vessel and bleached with H_2O_2 in the usual manner. This yields an excellent white of outstanding evenness. C.O.C.

Linseed Oil Sizing of Nylon Sleeving (X p. 84)

Contribution of Fluorescence to the Brightness of Papers Treated with Brightening Agents (XI p. 86)

VIII— DYEING

Fundamental Problems of Jig Dyeing
F. Martin and P. K. Woodward

Canadian Textile J., **77** (28 Oct 1960) 39–40
Differential diffusion of dyes through the cloth when it is batched on the jig roller, due to variable dye affinities and fabric tensions (from the centre to the outside of the batch), is postulated as a cause of ending and listing. Methods of minimising these faults are given. W.P.M.

Pad Mangle Processes
R. A. Peel *Dyer*, **124** (18 Nov 1960) 773–775
The apprentice needs to take constant care to avoid accidental errors in padding by standard methods. Six basic rules should be observed: protection from nip; standing bowls kept free of pressure, and clean; regular checks for wear on bowls; weekly maintenance; avoidance of nip damage; speed, pressure, temperature and volume must be known for every job. There is information on preparation, dyeing, finishing and water extraction of cotton, rayon and man-made-fibre piece goods. R.A.P.

Mechanism of the Acid Dyebath
M. Grindea *Ind. textilă* (Bucharest), **11** (3) (1960) 94–99
Chem. Abs., **54** (10 Oct 1960) 20211
The mechanism is characterised by formation of electrovalent bonds between the dye anions and the wool amino groups. Assuming wool to be $^+H_3NRCOO^-$, the dye RSO_3Na and the acid XH, then $^+H_3NRCOO^-$ combines first with the proton resulting from dissociation of the acid and with the anion X. $X^- \, ^+H_3NRCOOH$ in presence of the anionic dye RSO_3^- activates an ion exchange resulting in $RSO_3^- \, ^+H_3NRCOOH$, which is dyed wool. The affinity of wool for naphthalenesulphonic acid is $-8\cdot05$ kcal/mole. Introduction of an additional CH_3 group increases the affinity by $-0\cdot57$ kcal/mole, while a benzene ring increases it by $1\cdot37$ kcal/mole. Addition of a second sulphonic group reduces affinity by $1\cdot37$ kcal/mole. A lower pH favours diffusion of the dye in the fibre because the less stable H bonds facilitate creation of smaller dye particles and diffusion into the fibre. The electrokinetic potential established between fibre and solution is a function of pH and of the addition of a neutral electrolyte. While the quantity of an acid dye absorbed is a maximum at pH 3, that of a 1 : 1 chrome-complex is a maximum at pH 3–4. This is because with the chrome complex increase in concentration of H ions favours electrovalent bonds; further increase, however, weakens the coordinate bonds and favours desorption. 2 : 1 Complexes can be dyed at pH 6·0–6·5; higher pH improves levelling but not exhaustion. C.O.C.

Improved Method of Sulphur Dyeing
A. F. Moloskin

Byull. Tekh.-Ekon. Inform. Sovet. Narod. Khoz. Ivanovsk. Ekon. Admin. Raiona, (5) (1958) 13–14
Referat. Zhur. Khim., (1959) Abstr. No. 55812
Chem. Abs., **54** (25 Sept 1960) 18963
The amount of Na_2S necessary is reduced by half by adding 25–30 g/l. of waste mercerising lye. C.O.C.

Metal-complex Formation in Azoic Dyeing
—. Gross *Textil Praxis*, **15** (Oct 1960) 1046–1048
After brief discussion of requirements for metal-complex formation between dye and fibre, the author describes applications of recently developed Variogen bases (FH), suitable for azoic dyeing and for aftertreatment with metallic salts. When dyeing in a jig or on a winch, the metal salt can be added during coupling or soaping after-treatment. The metallic ions are derived from Cu, Co or Ni salts. Resulting dyeings are fast to light, wet treatments, and rubbing— they are unaffected by metal-sequestering agents. This novel method of complex formation is also applicable to continuous dyeing and printing. L.A.T.

New Horizons for Pigment Dyeing
N. S. Cassel *Canadian Textile J.*, **77** (28 Oct 1960) 45–52
The basic concepts of wetting, dispersion, rheology, expression, migration and drying are discussed in relation to an improved system of pigment–pad dyeing. Fastness of pigment dyeings is discussed in relation to the structure of the dye, binder, auxiliary products and fibre substrate. For all-round fastness the molecular structure of the dye must have a crystalline configuration with a minimum of polar groups. Initially the binder must contain polar groups to promote adhesion to the polar groups of the fibre, but unused polar groups in the binder and in the auxiliary products must be tied up on conversion of the binder to eliminate water sensitivity and promote high wash fastness; a reactive agent must be present to cross-link these polar groups. The binder must retain, after conversion, the necessary elastomeric properties to promote good rubbing fastness. The most suitable binders are emulsion polymers. A reactive agent which will cross-link with the ingredients and with the fibre has been developed. W.P.M.

New Aspects in High-temperature Dyeing of Cellulosic Fibres
A. Litzler and P. Ulrich

Textil Praxis, **15** (Oct 1960) 1048–1051
Advantages and drawbacks of high-temp. dyeing are discussed with special reference to vat dyes on cellulosic

fibres. During conventional high-temp. dyeing, hydrosulphite decomposes and many vat dyes undergo changes due to dehalogenation, hydrolysis of labile auxochromic groups, over-reduction, and isomerisation. The authors have overcome these difficulties by the use of a new reducing agent, Development Product HT (Ciba), and by pressurising the vessel with compressed air to about 3 kg/cm². The material was introduced at 30°C, the temp. raised to 120°C in 25 min, maintained for 5 min, and then the liquor was cooled to 60°C in 15 min. Dyeing was completed by conventional oxidation and soaping. 36 Dyes are listed which were successfully applied by this method.   L.A.T.

Concurrent Dyeing and Finishing of Cellulosic Fabrics
AATCC, Delaware Valley Section
> *Amer. Dyestuff Rep.*, **49** (31 Oct 1960) P 810–P 817
> (correction) *Ibid.*, **49** (28 Nov 1960) 889

Bright fast dyeings and excellent crease recovery are produced on cotton or rayon by a one-step pad–dry–cure procedure in which reactive dyes and urea–formaldehyde resins are applied simultaneously. Use of an alkaline catalyst permits rapid and effective fixation of both dye and resin, the dye being primarily attached to the cellulose and the resin completely polymerised. The method has proved successful under works conditions.   C.O.C.

Cold Dyeing with Reactive Dyes
P. Ulrich   *SVF Fachorgan*, **15** (Sept 1960) 570–581
Application of Cibacron (Ciba) dyes to natural and regenerated cellulosic fibres by the Pad–Roll method at room temp. is described. Advantages of this method are— simplicity, no intermediate drying, freedom from dye migration, good reproducibility of colour, and easy removal of unfixed dye from the fabric. The material is padded at 20–30°C with a soln. containing dissolved dye, urea, caustic potash, and Glauber's salt. After being batched, the rolls of padded fabric are revolved slowly for 10–16 h at 20–30°C, when fixation of the dye takes place. Residual alkalinity and unfixed dye are removed by washing in a jig or winch.   L.A.T.

Mechanism of Dyeing with Procion Dyes. I— Mechanism of Alkali Adsorption by Cellulose
H. H. Sumner   *J.S.D.C.*, **76** (Dec 1960) 672–678

Reactive Dyes and Cellulose Fibres
H. H. Sumner
> *J. Roy. Inst. Chem.*, **84** (Nov 1960) 389–390

A brief lecture report in which work is described which has led to the following picture of the reaction of Procion dyes with cellulosic fibres. Reaction takes place between dye and cellulose ions produced by neutralisation of cellulose by alkali; reactivity of cellulose ions appears to be similar to that of water ions. Procion dyes react to a greater extent with fibre than with water because the number of cellulose ions in the dyebath greatly exceeds the number of hydroxyl ions. Affinity and diffusion also play an important part by producing preferential adsorption of dye on the fibre.   M.T.

Dyeing Viscose Crêpes with Indigosols using Winch-dyeing Machine
É. R. Tsirule and V. F. Androsov
> *Tekhnol. tekstil. prom.*, No. 4 (17) (1960) 125–128

Affinity of Disperse Dyes for Cellulose Acetate
C. L. Bird; E. H. Daruwalla, S. S. Rao, and B. D. Tilak
> *J.S.D.C.*, **76** (Dec 1960) 680

Dyeing and Finishing Fabrics containing Tricel Triacetate Fibre
R. J. Mann   *J.S.D.C.*, **76** (Dec 1960) 665–672

Wool as a Fibre in Dyeing and Finishing
A. B. D. Cassie   *J.S.D.C.*, **76** (Nov 1960) 617–623

Black Dyeing of Persian Lamb Skins
F. Stather, H. Herfeld, S. Walther, and U. Stather
> *Ges. Abhandl. deut. Lederinst. Freiberg/Sa.*,
> (14) (1959) 115–129
> *Chem. Abs.*, **54** (10 Oct 1960) 20265

The normal commercial process uses a complex mixture of Logwood (C.I. Natural Black 1), Galls (C.I. Natural Brown 6), Sumac (C.I. Natural Brown 6), iron filings, Verdigris (C.I. Pigment Green 20), CuSO₄, FeSO₄, and NaCl. The colour is developed by air oxidation. A simplified dye bath has been developed which omits the Verdigris, the iron filings and either the Galls or Sumac. The skins are dyed for 24 h at 37°C, hung for 24 h in a damp atmosphere, and finally washed and neutralised.   C.O.C.

Benzyl Alcohol in Dyeing— II
H. Stern   *SVF Fachorgan*, **15** (Sept 1960) 582–583
Production of excellent navy blues and blacks with Cibalan (Ciba) dyes on nylon by jig dyeing using 4% (v/v) benzyl alcohol is described. The fabric is pretreated at 60°C in a liquor containing 4% benzyl alcohol at pH 4–5. After dissolved dye has been added, the bath is brought to the boil during approx. 10 passages of the fabric, and maintained at the boil during a further 14–16 passages. For blacks, aftertreatment with 0·5 g/l. each of Ultravon W (Ciba) and Calgon T (Benckiser) is recommended. Cuttings of jig-dyed fabrics illustrate the effect of benzyl alcohol.   L.A.T.

Constitution and Effectiveness of Organic Substances as Carriers in the Dyeing of Polyester Fibres with Disperse Dyes— II
P. Senner   *Textil Praxis*, **15** (Oct 1960) 1051–1056
For Part I see *ibid.*, **15** (Sept 1960) 940 (*J.S.D.C.*, **77** (Jan 1961) 42). 41 Substances, comprising derivatives of benzoic and salicylic acids, ketones, phenols, ethers, halogenated hydrocarbons, di- and tri-phenylmethane, and phenyl phenols were investigated. Dye uptakes, depicted graphically, were affected by the chemical constitution of the carrier. The effect of the substituent groups was studied and in a homologous series the carrier activity increased in this order $Br > Cl > NO_2 > OH > CH_3$. Reference is also made to the pH conditions and the quantity of an emulsifier in the system.   L.A.T.

Dyeing Faults in Polyester Fabrics
N. Bigler   *SVF Fachorgan*, **15** (Sept 1960) 591–596
Two faults, which became apparent after dyeing, are described and illustrated with photomicrographs. A navy blue cotton–polyester fabric showed stripiness in the warp direction. Microscopic examination revealed localised fibre fusion. The fault was brought about by irregular singeing due to maladjustment of the flame. The second example shows barry dyeing in 100% polyester fabric caused by severe mechanical abrasion of filaments in the warp yarn, which originated at some stage during weaving.
L.A.T.

PATENTS

Dyeing or Printing Cellulose Triacetate
BrC   *BP* 850,365 (26 July 1956)
Treatment with an aqueous acetone solution of a thiocyanate much improves the ability of cellulose triacetate to take up dyes. Thus cellulose triacetate fabric is dyed for one hour in acetone (containing 3% water) (60 ml), water (40 ml), NH₄ thiocyanate (10 g), and Cibalan Red 2GL (C.I. Acid Red 211) (1 g).   C.O.C.

Fast Dyeings on Vinylidene Cyanide Interpolymer Fibres
B. F. Goodrich Co.   *USP* 2,921,831 (13 Nov 1956)
NN-diphenylacetamide or *NN*-diphenylformamide are excellent carriers for application of basic or disperse dyes to vinylidene cyanide interpolymer fibres. Their use results in dyeings of depth and fastness comparable with those obtained with the same dyes on wool.   C.O.C.

Dyeing Plastic Sheeting
Pittsburgh Plate Glass Co.   *USP* 2,923,591 (4 Jan 1954)
Streakiness is avoided if the sheeting is stretched uniformly in both width and length before it is affixed to the frame on which it is immersed in the dyebath.   C.O.C.

Glycerine and its Compounds: Novel Applications (X p. 84)

Imparting Lustre to Suède Pigskins (XII p. 86)

IX— PRINTING

English Contribution to the Early History of Indigo Printing
P. R. Schwartz   *J.S.D.C.*, **76** (Dec 1960) 679

Influence of Intermolecular Changes of Maize Starch on its Properties as a Thickener for Vat Dye Printing Pastes
K. Dimov, R. Vulcheva, R. Gvozdieva, and E. Kalchev
> *Tekstil. prom.* (Sofia), **8** (9) (1959) 37–42
> *Chem. Abs.*, **54** (10 Sept 1960) 17890

Printing trials made with thickeners obtained by heating maize starch alone or with HCl and HNO₃ of various strengths at different temperatures and for

various times showed that the best results are obtained when the starch is heated alone at 140 or 150°C for 10 h, with HCl at 140°C for 3 h and at 150°C for 1 h, and with HNO_3 at 135°C for 3 h.   C.O.C.

Dye Compositions for the Multicolour Printing of Textile Fabrics by One Cylinder
L. Mühleisen   BP 850,310 (3 June 1958)

A printing block, preferably secured to a cylinder, has a layer of printing compositions composed of solid paste-like dyes corresponding to the pattern. The dye compositions used are obtained by mixing the leuco ester of a vat dye with ethylene glycol and glycerin and then adding a thickener and kneading the mixture into a solid paste. A suitable thickener consists of solubilised maize starch and Indian gum which has been dissolved in water and dried again. The thickener may also contain small amounts of dextrin and petroleum jelly.   C.O.C.

Vat Dye Printing Emulsions
United Merchants & Manufacturers
                                      BP 850,109 (27 Jan 1958)

A stable emulsion has a disperse phase consisting of a volatilisable hydrocarbon oil and as continuous phase an aqueous solution of a formaldehyde sulphoxylate reducing agent and a caseinate and/or soya bean proteinate. Presence of the caseinate or proteinate inhibits oxidation of the reducing agent.   C.O.C.

Fixing Vat and Sulphur Dye Prints
British Cotton Industry Research Association
                                      BP 848,792 (12 Nov 1955)

The material is printed, treated with a reducing agent, and then passed around a series of heated rotating cylinders. It is held against each cylinder by a travelling band of fluid-tight material and passes directly from the surface of one cylinder to that of the next cylinder. The temperature of the cylinders and their speed of rotation are such that the prints are fixed when they leave the last cylinder.   C.O.C.

Photographic Images on Paper or Textiles
North American Philips Co.   USP 2,923,626 (18 Sept 1956)

Paper or cloth is soaked in a solution of a light-sensitive compound, e.g. an alcoholic solution of p-methoxybenzene-diazocyanide. It is then exposed to light and treated with a solution containing mercurous ions, e.g. 0·01-N mercurous nitrate, and then with a physical developer, e.g. 0·5% metal, 2% citric acid and 0·2% $AgNO_3$. This yields a neutral grey copy of the negative. Alternatively the mercurous salt may be applied in the same solution as the light-sensitive compound. By using a colour-forming developer, e.g. those of USP 2,750,292, a dye image may be produced, followed, if desired, by removal of the metal image.   C.O.C.

Inhibiting the Fading of Cyan Dyes in Colour Photographs
General Aniline   BP 853,907 (U.S.A. 10 Jan 1957)

Treatment, before or after the final rinse, with a solution of a high-mol.-wt. cationic nitrogenous resin, e.g. Solidogen LT–13, and a water-soluble Ca, Sr, Mg, Zn or Cd salt, inhibits fading of cyan dye images which have been produced by use of a primary amino developer.

                            BP 855,629 (U.S.A. 10 Jan 1957)

Dye images formed from an oxidised colour developer and a phenolic colour former containing a long aliphatic chain are given a final rinse in a bath containing water-soluble salts of Ca, Mg, Zn or Cd.   C.O.C.

Metal-complex Formation in Azoic Dyeing (VIII p. 82)
Glycerine and its Compounds: Novel Applications (X this page)

X— SIZING AND FINISHING

Warp Sizing   Text. J. Aust., 35 (20 Aug 1960) 583 et seq.
Discusses the requirements of a good size and describes in detail sizes for rayon and synthetic-fibre warps based on eleven types of materials.   W.G.C.

Linseed Oil Sizing of Nylon Sleeving
P. Rochas and S. Pierret
     Bull. Inst. Text. France, (87) (Mar–Apr 1960) 91–95
            (correction) Ibid., (89) (July–Aug 1960) 105
Desizing of nylon fabric sized with linseed oil presents no difficulty if white yarns only are present. If the fabric also

contains coloured yarns, complete desizing may not be possible without impairing dyeings. Linseed oil should therefore not be used for sizing white nylon yarns which are to be woven in blends with dyed yarns.   J.C.F.

Migration of Non-substantive Solutes During Drying of Textiles
D. Wilson   J. Textile Inst., 51 (Oct 1960) P 590–P 603

Migration of non-substantive solutes such as crease-resist or drip-dry resins, resin-bonded pigments, sizes, and reactive dyes applied by padding, is very difficult to eliminate during the drying of textiles. With normal methods of drying, migration will occur if the regain of a fabric is above a certain critical value. To minimise migration the initial regain of the fabric must be reduced as far as possible by mechanical means. The fabric must then be dried in such a way that evaporation is equal at both surfaces. This does not eliminate migration from the inside of the fabric to the two surfaces, but may disguise its presence and prevent two-sided effects. The detailed study embraces drying by hot air, infrared radiation, hot cylinders, and (briefly) high-frequency electromagnetic field.   J.W.D.

Wet Crease-recovery
J. T. Marsh   J.S.D.C., 76 (Nov 1960) 629–630

Glycerine and its Compounds: Novel Applications
G. Machell   Text. Manuf., 86 (Oct 1960) 412–415

Glycerol (glycerine) and glycerol compounds find steadily increasing use in the textile and allied industries, forming the basis of several processes, including crease-resist treatments. Glycerol, glycerol diepoxide, diepoxides of glycerol–ethylene oxide condensate, glycerol borate, glycerol formals, monoglycerides, glycerol–urea–formaldehyde condensates, alkyd resins, alkyd resin epoxides and polyurethanes are used in textile finishing. Dyeing and printing processes can use glycerol, glycerol diepoxide and glycerol triacetate, whilst glycerol, monoglycerides and glycerol–ethylene oxide condensates can be used in anti-static treatments. Several water-repellent and flame-proofing processes are based on complex compounds of glycerol.   S.B.D.

Phenylmercury Compounds as Fungicides
E. Hoffmann and O. Georgoussis
       J. Oil Col. Chem. Assocn., 43 (Nov 1960) 779–786

Loss of fungal resistance of paints containing phenyl-mercury compounds as fungicides may be due to reaction with atmospheric traces of H_2S as, for example—

$$2C_6H_5HgR + H_2S \rightarrow (C_6H_5Hg)_2S + 2HR$$
$$(C_6H_5Hg)_2S \rightarrow (C_6H_5)_2Hg + HgS$$
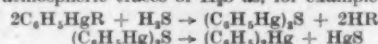
The end-products are of too low solubility to be effective as fungicides. Reaction may occur also with sulphur-containing pigments, with similar consequence—

$$2C_6H_5HgR + ZnS \rightarrow (C_6H_5Hg)_2S + ZnR_2$$

Pigments and extenders that do not contain sulphur do not destroy the fungicidal action of the phenylmercury compound. Data are given on the vapour pressure and solubility in water of phenylmercury acetate, chloride, and basic nitrate. The methods of determination are described.
                                              J.W.D.

Reaction of Cotton Cellulose with Epoxides in Presence of Acid Catalysts
J. B. McKelvey, B. G. Webre, and R. R. Benerito
       Amer. Dyestuff Rep., 49 (31 Oct 1960) 804–809

Those epoxides which are most reactive with cellulose under conditions of basic catalysis are practically inert with hydrogen ion catalysis. Thus ethylene epoxide and butadiene diepoxide give a large weight gain on cotton in presence of a base but only a slight gain in presence of hydrogen ion at room temperature in 20–24 h. Aqueous Zn fluoborate gives similar results, probably because of its hydrolysis in water, liberating hydrogen ion. The results are apparently equal to those obtained using a neutral salt solution. If Zn fluoborate or other latent Lewis acid catalyst is used at temperatures high enough to cause activation ($\ll$ 125°C), then in presence of some commercial epoxides the cotton is given durable crease recovery. However, while some diepoxides do impart dry crease recovery properties to cotton, not all diepoxides, e.g. resorcinol diglycidyl ether and diepoxystearic acid, do so. This discrepancy is probably caused by upset of the electrophilic balance of the epoxides in presence of large substituted groups. In addition, not all diepoxides add on

to the same extent. Yet in one case at least (butadiene diepoxide) better results, measured by crease angle, are obtained at low weight gains than at higher values. Vinylcyclohexene diepoxide gives similar results, though the difference is not as striking as in the former case. Furthermore, it is very difficult to explain the inertness of most monoepoxides toward cellulose in presence of Zn fluoborate. Only two monoepoxides, possibly because of their special structure, add on to cotton. It would be unreasonable to attribute the reactivity of diepoxides to an activated boron trifluoride–epoxy intermediate if such intermediate does not exist with a monoepoxide. Yet about 20 common monoepoxides fail to add to cellulose, let alone give crease recovery, by this method of catalysis. In addition some of these 20 compounds do add on in presence of a basic catalyst. Another anomaly is that some epoxides, e.g. 1,2-epoxydecane, do not add to cotton by any method of catalysis tried. Yet this molecule is not as large or as complex as some which do add on. The effect of BF_3 on cotton in absence of an epoxide is ruinous, yet in presence of epoxides or other crease-resisting compounds the weakening of the fibre is no greater than with the usual "safe" catalysts. Thus the true cause of loss in strength seems to be formation of a cellulose ether and/or deposition of polymer in the fibre. Comparison of the results of optimum base catalysis of diepoxides with cationic catalysis revealed that under basic conditions only wet crease recovery is imparted. No general theory of catalysis can be formulated at present for addition of an epoxide to cotton because either type is assumed to serve primarily as a ring opener and it is reasonable to expect that the products obtained— partly etherified cotton— would have reasonably identical properties.　　C.O.C.

Durability of Oil-repellency of Cotton Fabrics Imparted by Fluorochemicals

R. J. Berni, R. R. Benerito, and F. J. Philips
Text. Res. J., 30 (Aug 1960) 576–586

Of various perfluoro-metallic complexes and perfluoro-acrylates used as finishes, perfluoro-octanoic acid gave the best oil repellency after weathering tests. The finish was not fast to washing or dry-cleaning in presence of alkaline detergents and gave no protection against degradation in soil-burial tests. Padding with perfluorobutyl acrylate (< 10% solution) gave a lipophobic finish fast to a few washings with mild detergents. The finish had poor resistance to dry soiling compared with perfluoro-metallic finishes and gave no protection against degradation in soil-burial tests. Use of Al triacetate and perfluoro-octanoic acid gave best protection during soil burial but the finishes were not fast to washing. Lipophobic and hydrophobic finishes fast to washing are obtained when the perfluoro moiety is linked to cellulose by an ether linkage, only a very low degree of substitution being needed to give the desired repellencies and only a short perfluorinated chain being needed to impart hydro- and lipo-phobicity. When the perfluoro moiety contains an ω-H atom there is only low resistance to wetting by oil and water but good fastness to alkaline washing.　　C.O.C.

Movement of Wool Fibres in Fabrics during Felting, with Particular Reference to the Permanency of Pleats. III— Felting in a Woollen Fabric

K. R. Makinson　　*Text. Res. J.*, 30 (Aug 1960) 598–606

In some cloths, felting is caused principally by a mechanism for which the name "release" mechanism is proposed. Rootward migration of some fibres releases the mutual constraints between fibres, which then begin to recover from the state of strain imposed when they were twisted into helices during spinning. The net effect of limited untwisting by all the fibres in short lengths acting independently is contraction and widening of all the helices, with consequent shrinkage and thickening of the cloth. This mechanism was very important in a loomstate woollen cloth woven from single-ply yarn. It was much less important in loomstate worsted cloth woven from two-ply yarn, a construction which severely limits the extent of possible untwisting of the fibres. The closer packing of the fibres in worsteds also hinders untwisting. When the "release" mechanism is operative the fabric shrinks rapidly on washing, the shrinkage being considerable even when the degree of microfelting (rootward migration) is very small. Pleats are destroyed at a very low level of microfelting because very small longitudinal displacement

of any one fibre can trigger off untwisting movements in several fibres. Because of the rapid shrinkage occurring when the "release" mechanism is operative, Shorter's mechanism is not able to play as large a part in the shrinkage of woollens as of worsteds. Discussion of the characteristic feature of felting results in the proposal that felting should be defined as the process of progressive entanglement of the fibres in an assembly, occurring as a direct result of agitation by *undirected* external forces.
　　　　　　　　　　　　　　　　　　　　　C.O.C.

Improving the Abrasion Resistance of Cellulose Textiles

FBy　　　　　　　　　*BP* 851,289 (Germany 28 Sept 1957)

Treatment with an aqueous emulsion or organic solvent solution of a mixture of (1) a water-soluble polyester and a polyamide or (2) a water-soluble polyester and an alcohol-soluble mixed polyamide or (3) a water-soluble polyester and a *N*-hydroxyalkyl-, *N*-alkoxyalkyl- or *N*-alkthioalkyl-polyamide is followed by drying at > 100°C.　　C.O.C.

Imparting Dimensional Stability to Cellulose Materials exposed to Variations in Atmospheric Humidity

Upson Co.　　　　　　　　　　*BP* 849,522 (17 Dec 1956)

The material is impregnated with an aqueous salt obtained from a carboxylic acid containing at least one additional COOH group and/or alcoholic group and ammonia or a volatile amine. It is then heated to drive off the ammonia or amine. Thus viscose rayon gaberdine was impregnated with a 30% solution of NH_4 diethyleneglycol disebacate. After drying, the cloth contained 37% stabiliser and showed a reduction of 94% in warpwise and 100% in weftwise expansion–contraction caused by variations of 0–90% in r.h. 66 Examples are given, including application to paper and regenerated cellulose film.　　　　　　　　　　　　　　　　　　C.O.C.

Resin Finish

British Industrial Plastics　　　　*BP* 849,411 (18 Dec 1957)

An aqueous solution of a urea–formaldehyde condensate which comes out of solution before, on dilution, the strength of the solution becomes 10%, is diluted with water in presence of a hydrophilic colloid. The resulting dispersion is used for impregnating textiles. Thus maize starch (70 parts) was made into a clear aqueous solution with a little water. An 80% aqueous solution of a urea–formaldehyde resin (1 : 1·7) which would precipitate if kept overnight after diluting with twice its weight of water at 15°C, and tartaric acid (0·5) was prepared. The two solutions were mixed and then diluted with water to yield a product containing 80% resin solution (70 parts), maize starch (70), tartaric acid (0·5), and water (to bring to 1000). Cotton and viscose rayon cloths padded with this mixture and cylinder-dried at 100°C acquired a stiff finish fast to washing and requiring no further processing.　C.O.C.

Improving the Resistance to Wet Treatment of Finishes obtained by use of Water-sensitive Agents

ICI　　　　　　　　　　　　*BP* 849,368 (24 June 1957)

Finishing agents containing free hydroxy or amino groups, e.g. starch, cellulose ethers, polyvinyl alcohol and octadecylamine, are applied at pH 7 in presence of a non-self-condensable non-fluorescent mono- or di-halogeno-1,3,5-triazine. Thus cotton limbric is impregnated with a solution containing sago starch (7·5 per 100 parts of water), Na 2- (4,6 - dichloro - 1,3,5 - triazin - 2 - yl) - amino-naphthalene-6-sulphonate (0·5) and $NaHCO_3$ (0·75) and then without being dried is heated for 8 min at 110°C. Finally it is given a soap boil. The treated cloth has a fuller and firmer handle than one treated with starch alone and soap-boiled.　　　　　　　　　　C.O.C.

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Spectrometric Investigations of Cellulose. I— Influence of Moisture on the Infrared Spectrum of Cellulose
O. Ant-Wuorinen and A. Visapää

Paperi ja Puu, 42 (June 1960) 367–372 (*in English*)
A new sandwich technique is suggested for obtaining better infrared spectra of cellulose, taking into account all the functional groups of cellulose at their corresponding wavelengths. Work is in progress to correlate infrared and chemical methods for determining the functional groups of cellulose.   R.A.

Influence of Relative Humidity on the Crystallinity of Cellulose
O. Ant-Wuorinen and A. Visapää

Paperi ja Puu, 42 (Oct 1960) 515–517 (*in English*)
Experiments with three types of cellulose at three different r.h. showed that an increase in r.h. causes lowering of the crystallinity index and *vice versa*. It is suggested that dry cellulose contains more cellulose–cellulose hydrogen bridges than does wet cellulose in which cellulose–water–hydrogen bridges predominate. The change in crystallinity can be followed by means of infrared spectra.   R.A.

Chain-folding— A Possibility to be Considered in Connection with the Cellulose Molecule
B. A. Tönnesen and Ø. Ellefsen

Norsk Skogindustri, 14 (July 1960) 266–269
The theory of chain-folding, i.e. the bending over of the chain when it reaches a certain length, turning back on, and crystallising with, itself, already confirmed experimentally for nylon and polyethylene, is applied to native and mercerised cellulose. It is suggested that the chains fold in a plane parallel to the 101 plane. This would not disagree with established X-ray data for cellulose and would explain observed DP values. 15 References.
    R.A.

Influence of γ-Cellulose on Brightness Reversion at High Levels of Oxidation
O. A. Kaustinen and N. A. Jappe

Paperi ja Puu, 42 (Sept 1960) 485–490 (*in English*)
The specific absorption coefficient, taken as a measure of reversion, is not much affected by the γ-cellulose content of the pulp and appears to be independent of the copper number over the range 10–40. The nature of the long-chain fractions of the pulp is of decisive influence on the yellowing tendencies of pulps oxidised to copper number values above 10 by periodic acid.   R.A.

Contribution of Fluorescence to the Brightness of Papers Treated with Brightening Agents
F. Grum and T. Whightman

Tappi, 43 (May 1960) 400–405
By reversing the optical path and providing a suitable light source, a Beckman DK–2 Spectroreflectometer can be modified for the measurement of the brightness of samples containing fluorescent brightening agents. The brightness of the sample is expressed by the max. emittance value and the wavelength at which it occurs, together with a parameter describing directly the contribution of the fluorescence radiation to the complete radiation, and which is independent of the source of illumination.   R.A.

PATENTS

Coating Composition for Paper
S. D. Warren Co.   BP 854,501 (U.S.A. 16 Jan 1956)
An aqueous pigment dispersion contains a binder and a metal complex whose metal ions are released by application of formic acid, causing the binder to gel. The formic acid is then evaporated during drying of the coated paper.   R.A.

Coated Paper
S. D. Warren Co.   BP 854,500 (U.S.A. 16 Jan 1956)
Provision of a long nip allows operating temperatures above the b.p. of the liquid component of the composition without disruption of the coating, so that drum-finished paper can be produced at much higher speeds than previously.   R.A.

Manifolding Papers
Caribonum   BP 852,131 (9 Apr 1956)
When making manifolding papers by the process of BP 849,103, the transferable coating includes as the first reactant at least one N-substituted mono- or di-leucauramine, e.g. phenyl-leucauramine and o-ditolylene-p-dileucauramine. These compounds are non-odorous, non-toxic, and remain almost colourless when exposed to light or oxidants.   C.O.C.

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Imparting Lustre to Suède Pigskins
F. Stather, H. Herfeld, H. Moser, and K. Härtewig
Ges. Abhandl. deut. Lederinst. Freiberg/Sa., (14) (1959) 77–86
Chem. Abs., 54 (10 Oct 1960) 20264
Colour is levelled and deepened by application of sulphated oil of low "water penetration number", soap emulsions of linseed or olive oil, aqueous solutions of gelatin or HCHO, or very small amounts of pigmented nitrocellulose lacquer. Application of a pigmented casein finish is much less effective and that of basic dyes, organic solvents, or highly sulphated oils is unsatisfactory.
    C.O.C.

PATENT

Tanning
YDC   BP 854,431 (11 Feb 1958)
A mixture of a water-soluble or water-dispersible urea-formaldehyde condensate and a water-soluble salt of an inorganic iso- or hetero-polyacid whose free acid can exist in colloidal or macromolecular state, e.g. sodium hexametaphosphate, can be used at $15–25°C$ and pH $2·5–3·0$ to yield an excellent leather.   C.O.C.

Fibre Formation from Solutions of Collagen (VI p. 81)
Black Dyeing of Persian Lamb Skins (VIII p. 83)

XIII— RUBBER; RESINS; PLASTICS

Stereoregular Polymers. VI— Copolymerisation with Ziegler Catalysts
S. Murahashi, S. Nozakura, and M. Sumi

Bull. Chem. Soc. Japan, 33 (Sept 1960) 1170–1174
Binary copolymerisation of styrene, allyltrimethylsilane, and 3-butenyltrimethylsilane, is investigated, using the Ziegler catalyst $(Al(C_2H_5)_3–TiCl_4$ in n-heptane) at $70°C$, and previously described technique (*ibid.*, 32 (1959) 1094). The separation is described of the cryst. part of the copolymers obtained into two kinds of genuine cryst. copolymers, each of which has an extremely different composition from the other. The nature of the active sites on the catalytic surface is discussed to elucidate this fact. The constitution of the individual cryst. fractions appeared to vary case by case, i.e. some were block copolymers and others random copolymers.   H.H.H.

Studies on Epoxy Compounds of Higher Fatty Acids and their Derivatives. II— Preparation of Metal Epoxystearates
Y. Suhara   *Repts. Govt. Chem. Industr. Res. Inst., Tokyo*, 55 (Aug 1960) 283–286
Metal epoxystearates were obtained in good yield by treating 9,10-epoxystearic acid with Ba, Ca, Co, Mn, and Zn acetates in ethanol solution. 9,10-Epoxystearic acid and barium epoxystearate were found to increase the thermal stability of polyvinyl chloride resin.   M.T.

Ageing of Plastics— II
P. Dubois and J. Hennicker

Plastics, 25 (Nov 1960) 474–478
To those external influences promoting deterioration on ageing that were discussed in Part I (J.S.D.C., 77 (Jan 1961) 49) are added others of mechanical, electrical, and environmental origin. Anticipation of ageing and the preventative steps that can be taken in consequence are briefly considered. Factors that can influence ageing and that can be varied during preparation of the materials are also discussed; these include the control of orientation (through stretching, non-oriented injection, and addition of a second, non-cryst. polymer), and the reduction of internal stress by additives such as plasticisers, fillers, and the

like, or the introduction of side-chains or branching into the polymer itself. The basis, conditions, and usefulness of accelerated ageing tests are considered and available methods are outlined. Factors promoting ageing are tabulated together with methods by which they can be evaluated; surface and volume ageing must be separately considered.　　　　　J.W.D.

Bacterial Attack on Rubbers and Plastics

Rubber & Plastics Age, **41** (Nov 1960) 1366–1367

When dissimilar materials such as polyvinyl chloride and a fabric are brought together, susceptibility to attack by micro-organisms is increased. A brief, illustrated account is given of the use of pentachlorophenyl laurate to suppress bacterial attack; it is compatible with and will protect both phases of coated fabrics such as automobile upholstery, conveyor belting, and fire hose.　　　　　J.W.D.

PATENT

Reducing the Maturing Time of Linoleum Compositions

ICI　　　　　　　　　　BP 855,209 (31 Mar 1958)

Addition of aliphatic aminosulphonic acids (aliphatic of 1–6 C) reduces the maturing time of linoleum compositions, causes no significant hardening during mixing and yields a sheet of good colour and uniform hardness.
　　　　　C.O.C.

XIV— ANALYSIS; TESTING; APPARATUS

Precision in Interlaboratory Tests

W. S. Connor　　　*Ind. Eng. Chem.*, **52** (Oct 1960) 71A–73A

To illustrate sources of variation occurring in interlaboratory tests, 256 samples of wool–cotton–viscose rayon fabric cut from a single blanket were allocated to four laboratories and tested in each for wool content by measuring alkali and acid solubility. Two runs for each method in each laboratory were carried out at different times. Statistical analysis showed no variation in wool content within the blanket. Significant differences between the average results for the four laboratories were found. Precision of tests in each laboratory, indicated by the square of the standard deviation of the results, varied and average values of each test differed significantly from run to run. There was little basis of choice between the two methods with respect to precision.　　　　　F.J.

A.A.T.C.C. Technical Committee on Research— 202nd Meeting

Amer. Dyestuff Rep., **49** (19 Sept 1960) P 701–P 706

A review of recent work of many of the A.A.T.C.C. committees responsible for developing standard methods of test. Subjects include antibacterial agents, colour fastness, colour measurement, identification of finishes, resistance to insect pests, resistance to staining and soiling, wash-and-wear testing, weathering, odours in resin finishing, and evaluation of creasing.　　　　　M.T.

Chromatography of Dye Intermediates. XI— Chromatographic Separation and Identification of Naphthalenesulphonic Acids

J. Latinák　　　*Collection Czechoslov. Chem. Communs.*,
　　　　　　　25 (1960) 1649–1655 (*in German*)
　　　　　　　Chem. Abs., **54** (25 Sept 1960) 18449

Both the 1- and 2-naphthalenemonosulphonic acids and some isomers of naphthalene di- and tri-sulphonic acids were separated on S. and S. No. 2043a paper by descending chromatography in 1:3 conc. aq. HCl–water and two-dimensional ascending chromatography in 2:1 propanol–aq. ammonia and then in 1:3 conc. aq. HCl–water with Pinakryptol Yellow as detecting agent (R_f values given). The 2,6- and 2,7-naphthalenedisulphonic acids were separated, identified by fusion with NaOH (to give the corresponding 2-naphtholsulphonic acids) and chromatographed on Whatman No. 4 paper (impregnated with 5% aq. $NaHCO_3$) in 2:1 propanol–aq. $NaHCO_3$ with diazotised *p*-nitroaniline as detecting agent.　　　　　C.O.C.

Infrared Analysis of Dyes. III— Red Food Dyes and Rhodamine B

M. Suzuki, E. Nakamura, and Y. Nagase
　　　　　　　Yakugaku Zasshi, **80** (1960) 916–919
　　　　　　　Chem. Abs., **54** (25 Oct 1960) 21764

Infrared spectra were measured of the following dyes used for foodstuffs in Japan: Ponceau 3R (C.I. Food Red 6), Amaranth (C.I. Food Red 9), Erythrosine (C.I. Food Red 14), Ponceau SX (C.I. Food Red 1), Oil Red XO,

Ponceau R (C.I. Acid Red 26), New Coccine (C.I. Food Red 7), Eosine (C.I. Acid Red 87), Phloxine (C.I. Acid Red 98), Rose Bengal, and Acid Red, together with one, Rhodamine B (C.I. Food Red 15), which is not used in Japan as a food dye. Each could be identified in a limit of 40–300 γ by the characteristic bands. Attempted quantitative determination of Rose Bengal and Rhodamine B showed that the former could be determined by a characteristic band at 961 cm^{-1} with standard deviation 0·519 and Rhodamine B by one at 1078 cm^{-1} with standard deviation of 0·633. A mixture of these two dyes gave results to within a standard deviation of 0·624 for Rose Bengal and 0·659 for Rhodamine B.　　　　　C.O.C.

Accelerated Fading of Certified Dyes in Presence of Non-ionic Surfactants

M. W. Scott, A. J. Goudie, and A. J. Huettman

J. Amer. Pharm. Assoc., Sci. Ed., **49** (1960) 467–472

FD&C Red No. 1 (C.I. Food Red 6) (I), FD&C Blue No. 2 (C.I. Food Blue 1) (II), FD&C Red No. 4 (C.I. Food Red 1), FD&C Green No. 1 (C.I. Food Green 1), FD&C Yellow No. 5 (C.I. Food Yellow 4), and D&C Orange No. 3 (C.I. Food Orange 4) and the following surfactants, Tineen 20, Igepal CA–710, Pluronic F–68 (III), Myrj 52 and Brij 35 (IV), were studied for colour fastness in aqueous buffered solutions. In all but 4 of the 30 systems tested accelerated fading was observed compared with that of solutions of the dyes alone. For mixtures of I and IV and of II and III, the rate of fading followed pseudo first-order kinetics.　　　　　C.O.C.

R_f Values and Electrophoretic Mobilities of Some Anthraquinone Derivatives

J. Chromatography, **4** (Nov 1960) D30–D32

R_f values of 68 anthraquinone deriv. containing mainly amino, hydroxy, halogeno, nitro, sulphonic or disulphochloride groups are listed from J. Franc and M. Wurst, *Collection Czechoslov. Chem. Communs.*, **25** (1960) 657. Whatman No. 1 paper impregnated with 30% liquid paraffin in benzene was used in a descending method with 80% ethanol as solvent. Detection was by U.V. or visible light. Electrophoretic mobilities in 3-N NH_4OH and N CH_3COOH of most of these compounds are given.　　　　　F.J.

Identification of Organic Compounds. XXXV— Paper Chromatography of Solvent Dyes

J. Gasparič and M. Matrka
　　　　　Collection Czechoslov. Chem. Communs.,
　　　　　　　25 (1960) 1969–1972 (*in German*)
　　　　　　　Chem. Abs., **54** (25 Oct 1960) 20670

23 Solvent dyes and related compounds were chromatographed on Whatman No. 3 paper impregnated with petroleum, medicinal paraffin, dodecyl alcohol and $HCON(CH_3)_2$. The R_f values in various solvent systems (ethanol–water, ethanol–aq. ammonia, cyclohexane) are tabulated.　　　　　C.O.C.

Determination of Coal-tar Colours on Oranges. Determination of Oil Red XO in Presence of Citrus Red No. 2 (C.I. Solvent Red 80)

W. Przybylski, R. B Smith, and G. G. McKeown
　　　　　J. Assoc. Off. Agric. Chem., **43** (1960) 274–278
　　　　　　　Chem. Abs., **54** (25 Sept 1960) 18824

Method for separating extracted colours, after preliminary purification, by reverse-phase paper chromatography and individual electrophotometric determination. It applies to Oil Red XO (1-xylylazo-2-naphthol) (now prohibited in Canada and the U.S.A.) and to Citrus Red No. 2 (1-(2,4-dimethoxyphenylazo)-2-naphthol) (now permitted in Canada and the U.S.A. for colouring oranges), as also to other synthetic dyes. Direct chromatography of colour extracts provides a simple qualitative method for rapid screening of samples, which will detect as little as 0·03 p.p.m. of a given dye on oranges. A spectrophotometric method is outlined for the rapid determination of Oil Red XO in presence of Citrus Red No. 2.　　　C.O.C.

Chromatographic Qualitative Analysis of Oxidation Bases

N. V. Grigor'eva
　　　*Issledovaniya v Oblasti Ionoobmen. Raspredelitel.
　　　i Osadoch. Khromatog., Akad. Nauk. S.S.S.R.,
　　　Otdel. Khim. Nauk.*, (1959) 134–137
　　　　　Chem. Abs., **54** (10 Oct 1960) 20212

Preparation of reagents and silica gel for the chromatographic analysis of oxidation bases is described. Colour

plates show the characteristic chromatographic patterns of p-phenylenediamine, pyrocatechol, pyrogallol, 4-nitro-o-phenylenediamine hydrochloride and dimethyl-χ-phenylenediamine (C.I. 76060, 76500, 76515, 76021, and 76075). C.O.C.

Determination of Oils, Fats, and Waxes in Cotton (T.T.S. No. 65)
Textile Institute

J. Textile Inst., 51 (Nov 1960) P 660–P 662

Cotton textiles may contain oils, fats, and waxes derived from the raw cotton itself or from sizing and finishing agents. These materials are usually soluble in organic solvents; this method uses methylene chloride for grey, scoured, and bleached cotton, and light petroleum (40–60°C) for textiles dyed or printed with vat or azoic dyes. Complete extraction is not necessarily achieved, but the amounts extracted are reproducible and serve to characterise the cotton sufficiently for practical purposes. Cotton textiles containing oxidised unsaturated oils, water-proofing or softening agents based on cetylpyridinium halides, rot-proofing agents, and synthetic resins cannot be tested by this method. M.T.

Determination of Oils, Fats, and Waxes in Wool (T.T.S. No. 64)
Textile Institute

J. Textile Inst., 51 (Nov 1960) P 657–P 660

Wool textiles may contain (a) wool grease, (b) oils added to assist processing, (c) detergents taken up during scouring, and (d) finishing agents. Estimation of these substances is important for determining clean wool content. They cannot be estimated individually by solvent extraction, so that it is only possible to determine the total amount extracted by a given solvent under specified conditions, additional information being obtained by analysis of the extract. In this method a conditioned, weighed specimen is Soxhlet-extracted with diethyl ether and the amount extracted is expressed as a percentage of the original weight. It is recognised that the procedure does not necessarily completely remove all fatty matter present. M.T.

Determination of Moisture in Wool with Karl Fischer Reagent
J. R. Wilson and M. M. Sandomire

Text. Research J., 30 (Aug 1960) 587–591

Formamide is a powerful dehydrating agent capable of dehydrating activated alumina, silica gel and other such desiccants. When used as the water-extracting solvent in the Fischer method it ensures complete extraction of water from wool with minimum of heating. Interfering substances give little or no trouble. With two samples a precision of ± 0·1% is attained, and with seven a precision of ± 0·05%. Moisture in cloth is best determined with squares of cloth rather than ground material, as grinding changes moisture content in an unpredictable, irregular manner. The method is suitable as a calibration method for physical determinations of moisture in wool. C.O.C.

Weathering of Textile Yarns
M. Fels *J. Textile Inst.*, 51 (Nov 1960) P 648–P 656

Orlon, nylon, Terylene, viscose rayon, secondary cellulose acetate, cellulose triacetate, and cotton yarns of approx. 400 denier (45 tex) and wool yarn of approx. 860 denier (96 tex) were wound on aluminium alloy frames and exposed at Didcot, England, and Kano, Nigeria, for 80–112 and 120–200 days, respectively. Orlon (continuous-filament) had a much better resistance to weathering than any of the other fibres, which deteriorated rapidly on exposure at Kano. At Didcot the dull nylon, viscose, and acetate yarns degraded more easily than the bright yarns. The behaviour of the nylon and Terylene yarns was of interest because of their use in Service clothing. Under tropical conditions they behave similarly. Cotton lost strength slowly compared with the other cellulosic fibres. It is suggested that more consideration should be given to comparing retained strengths, since in some instances the percentage retained strength might be misleading. M.T.

Resistance of Textile Fibres to Weathering— II
J. Lünenschloss and H. Stegherr

Textil Praxis, 15 (Oct 1960) 1011–1017

In this second part of the paper (Part I: *ibid.*, 15 (Sept 1960) 931–939; J.S.D.C., 77 (Jan 1961) 51) the load–extension curves (26 diagrams) are shown for various yarns in the original state and after 3, 6, 9, and 12 months of weathering. The elastic modulus of cellulosic fibres increases on weathering. The converse is true in the case of polyamide fibres. Acrylics show good stability and resistance to weathering. The above results are also expressed (8 diagrams) as changes in the work modulus in relation to the duration of weathering. Changes in the resistance to abrasion and bending have also been studied and are depicted graphically. L.A.T.

Identification of Unknown Synthetic Fibres. IV— Revision, New Fibres, Cross Sections
S. G. Smith

Amer. Dyestuff Rep., 49 (17 Oct 1960) 774–782

Seventeen new fibres of various chemical types are added to those already included in the first three papers in the series. The fibres are separated into five groups by examination in polarised light. Confirmatory tests are given to aid the identification of individual members of these groups; the tests include determinations of micro-fusion point, solubility, and density. Sketches of typical cross sections (in outline only) of 41 fibres are given. J.W.D.

Infrared Spectroscopic Investigation of Nature of Bonds of Moisture in Gelatin and Photographic Emulsions
L. A. Lepilkina

Kolloid zhur., 22 (July–Aug 1960) 411–417

Using electrophysical measurements and infrared spectroscopy, the changes in bonds between moisture and gelatin, and between moisture and photographic emulsions during drying, have been studied. The principles involved in structural changes during drying have been established and the best drying method developed. L.S.L.

Infrared Spectroscopic Investigation of the Adsorption of Water on a Hydrated Silica Gel Surface
A. V. Kiselev and V. I. Lygin

Kolloid zhur., 22 (July–Aug 1960) 403–410

The infrared absorption spectrum of water adsorbed on a silica gel, at a stage when a monolayer has been formed and condensation starts taking place, was studied. With the formation of a monolayer, there is a decrease in absorption at frequencies absorbed by hydrated silica and an increase in absorption characteristic of hydroxy groups deformed by hydrogen bond formation. This confirms that the water is attached by hydrogen bonds and that hydroxy groups of hydrated silica gel are basic points for physical adsorption of water. The possibilities of using the spectroscopic methods for investigation of thermo-dynamic properties of adsorption systems are also discussed. L.S.L.

Effect of Fluorescent Brightening Agents on the Light Fastness of Dyed Cellulose
C. H. Giles and S. M. K. Rahman

J.S.D.C., 76 (Dec 1960) 681

Evaluation of Finishes for Resistance to Staining and Soiling
H. B. Goldstein

Amer. Dyestuff Rep., 49 (3 Oct 1960) P 740–P 741

Review, by chairman of A.A.T.C.C. Committee RA 56, of its work. Two task groups deal, respectively, with (a) oil-borne stains and (b) wet soiling. The first group has not yet been able to establish satisfactory correlation weebetn laboratory test methods and practical soiling resistance. The second group has shown that most "wash-and-wear" finishes wet-soil less than untreated cotton. M.T.

An Autoradiographic Method Based on Tritium for Locating Resin Finish in Textiles
G. S. Park J.S.D.C., 76 (Nov 1960) 624–629

Spectrometric Investigations of Cellulose. I— Influence of Moisture on the Infrared Spectrum of Cellulose (XI p. 86)

XV— MISCELLANEOUS

Assessment of "Softness" in a Synthetic Detergent by Biological Means (VII p. 81)

APPOINTMENTS etc

Advertisements relating to APPOINTMENTS VACANT, APPOINTMENTS WANTED, and MISCELLANEOUS are invited for insertion on this page. Advertisements of Appointments Wanted are gratis to members, but must not exceed twenty-four words.

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Replies may be addressed BOX—, THE SOCIETY of DYERS and COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE, where all communications relating to these Advertisements are treated in strict confidence.

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Principal— Dr. W. E. Scott, M.B.E.

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Salary (Burnham Scale)— £700 p.a. by £27 10s p.a. to £1150 p.a. There are additions for approved qualifications and training and the commencing salary may include increments for approved industrial experience.

Forms of application and further particulars obtainable from the Principal, to whom applications should be returned without delay.

H. GRAY

15th January 1961   *Clerk to the Governors*

THE COTTON, SILK AND MAN-MADE FIBRES RESEARCH ASSOCIATION

(SHIRLEY INSTITUTE)

ABSTRACTORS are required for the Information Department. Applicants, who should be science graduates, and preferably, but not essentially, have knowledge of textile technology, must be capable of abstracting technical and scientific papers from foreign periodicals. The initial salary offered will depend upon qualifications and experience, and will carry superannuation under the Federated Superannuation System for Universities. Applications, giving all relevant details, in handwriting, should be addressed to The Director, B.C.I.R.A., Shirley Institute, Didsbury, Manchester 20.

APPLICATIONS are invited for post of Dye Works Manager with a large and progressive Midlands Organisation. Must have a sound practical and technical knowledge of yarn and knitted fabric dyeing and be a capable organiser. Excellent future prospects for suitable applicant who should be between the age of thirty and forty years. Reply in confidence to Messrs. Pole, Russell & Co., Chartered Accountants, 2 Salisbury Road, Leicester.

GERARD BROTHERS, New Basford, Nottingham, have a vacancy for a Representative to sell soaps to the Textile Industry in Yorkshire and Lancashire. Applications stating age and experience should be made to the Managing Director.

SKETCHLEY LIMITED have a vacancy for a Chemist in their central laboratory at Hinckley, Leicestershire. He should be a Science Graduate or an Associate of the Society of Dyers and Colourists, and some practical experience in the application of dyes to textiles will be an advantage. The position carries an attractive salary and prospects of advancement. Housing assistance available if required. Applications should be made to Miss D. M. Haslam, Personnel Manager.

APPOINTMENTS WANTED

DIPLOMA in Textiles, age 25, now doing research in dyeing at Leeds University, little practical experience, mainly wool, seeks position with scope for learning, anywhere in England. Available July. Box W647

MISCELLANEOUS

ADVERTISER has surplus stocks of direct dyes for sale. Replies to Box M109.

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Midland Hotel   Manchester

BRISTOL SYMPOSIUM
20 21 22 September 1961
Grand Hotel   Bristol

LONDON LECTURE
20 October 1961
Waldorf Hotel   London

MERCER LECTURE
17 May 1961
Midland Hotel   Manchester

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